Author:
Bowen, Lucy Elizabeth

Title:
New Reactions and activation methods in Olefin Trimerisation Catalysis

New Reactions and Activation Methods in Olefin Trimerisation Catalysis

University of BRISTOL

Lucy Elizabeth Bowen

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Abstract

This thesis describes new catalytic reactions, new activation methods and new ligand derivatives based on chromium *N,N*-bis(diarylphosphino)amine (PNP) olefin trimerisation catalysts. Chapter 1 presents an introduction to this area. The main differences between non-selective olefin oligomerisation and selective trimerisation are discussed, as well as the commercial uses of LAOs. The mechanism of trimerisation and a survey of successful catalyst systems is given, with particular emphasis on PNP ligands. More recent advances such as selective tetramerisation are discussed.

Chapter 2 describes the use of chromium PNP catalysts for the cotrimerisation of ethene and other alkene monomers, particularly styrene. The effect of temperature, reaction time, comonomer concentration and ligand structure are investigated and a mechanism scheme is proposed. The cotrimerisation of ethene and styrene was found to form phenylhexene, with the ligand **1** system giving predominantly 1-phenylhexene isomers **50** and **51**, with a TOF of 2468 h^{-1}. Other PNP ligands tested gave 3-phenylhexene isomers **55** and **56**. The trimerisation of isoprene using the same chromium PNP systems is explored in Chapter 3. Using the ligand **1** system, the trimerisation of isoprene produced isomers of 2,6,11-trimethyldodecatetraene, 1,5,10-trimethyl-1,5,9-cyclododecatriene and higher isoprene oligomers, with a productivity of 826 g (g Cr h)$^{-1}$. Other PNP ligands tested produced the same products as ligand **1** with differing productivities. Some of the results from these two chapters have been published.[93, 130]

Chapter 4 describes the use of chromium(I) PNP carbonyl complexes for the oligomerisation of ethene. The syntheses and structures of $[Cr(CO)_4(\mathbf{1})]$, $[Cr(CO)_4(\mathbf{19})]$, $[Cr(CO)_4(\mathbf{5})]$ and $[Cr(CO)_4(NO)(\mathbf{1})]$ are reported. These compounds were then tested for ethene trimerisation by activation with an oxidising agent with a weakly coordinating anion, $[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$ and a CO scavenger, $AlEt_3$. The results from this chapter have been published.[160] A series of novel PNP and dppe based ligands with *ortho* oxygen donors on the phenyl rings were also synthesised and tested for ethene trimerisation, as described in Chapter 5. Finally Chapter 6 gives experimental details for the preceding chapters.

Acknowledgements

First I would like to thank Dr Duncan Wass for being a great boss and employing me for the past three years. Then there is my group past and present: Rich, Igor, Eleanor, Steve, Mindy, Tom, Tim, Andy and Jorge. They have put up with me bossing them around for three years, making then clean the lab and do the washing up. A special thanks to my project student Nan, who worked hard on the Isoprene Trimerisation project; without her help, this would not have been such a success. Thanks to Steve Mansell and Mairi Haddow for solving my crystal structures. Not forgetting Gareth and his group and past project students: Christian, Mike, Ka Man, Steve, Karl, Andy and Mike C. Also thanks to the Pringle, Russell and Bedford groups.

Thanks to my family, Dad, Mum and Amy. Mum for always listening to me ranting down the phone when things were tough. Dad for giving me support and trying to understand what it is I actually do. Then there is Tafi, Jake, Moss, Gizzy, Tom, Bertie, cattle, sheep, ducks and geese for giving me a distraction from chemistry. Vicky, Katie and Laura you were brilliant flatmates, making the past three years great fun!!

I would like to dedicate this thesis to my Uncle George, who is sadly unable to see me finish my PhD. Leaving home for the first time to do my undergraduate degree was a large step for me; it was made easier by having my own personal taxi service (driven in style) between university and home. He was always interested in what I was doing and offered encouragement in whatever I did and I miss his input and help. I hope he is proud of what I have achieved.

Declaration

The work described in this thesis was carried out in the School of Chemistry, at the University of Bristol, under the supervision of Dr Duncan Wass between October 2004 and February 2008. The work is original except where indicated and has not been submitted for any other degree. The views expressed are those of the author and in no way represent those of the University of Bristol.

Lucy Bowen

University of Bristol

February 2008

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Abbreviations

acac	Acetylacetonate
Ar	Aryl
BuAO	Butylaluminoxane
COD	1,5-Cyclo-octadiene
Cy	Cyclohexyl
DEAC	Diethylaluminium Chloride
DMB	2,3-Dimethyl-1,3-butadiene
Dppe	Bis(diphenylphosphino)ethane
Dppm	Bis(diphenylphosphino)methane
EA	Elemental Analysis
EAO	Ethylaluminoxane
Et	Ethyl
GC	Gas Chromatography or Gas Chromatogram
GC-MS	Gas Chromatography-Mass Spectroscopy
*i*Pr	Isopropyl
MAO	Methylaluminoxane
Me	Methyl
MMAO	Modified Methylaluminoxane
MS	Mass Spectroscopy
NBD	Norbornadiene
NMR	Nuclear Magnetic Resonance
Ph	Phenyl
RT	Room Temperature
*t*Bu	Tertiarybutyl
TEA	Triethylaluminium
TMA	Trimethylaluminium
TMCD	Trimethylcyclododecatriene
TMD	Trimethyldodecatriene
TOF	Turnover Frequency

Other abbreviations are given in the text.

Chapter 1

Introduction

1.1. Linear α-Olefins

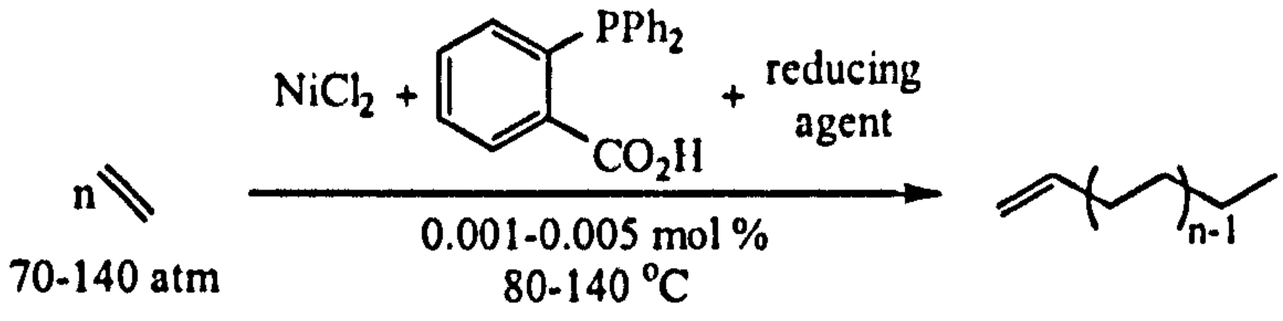
The oligomerisation of ethene to give linear alpha olefins (LAOs) is of great interest in industry. Linear α-olefins (LAOs) or 1-alkenes, with a carbon range of C_4-C_{20}, have a large number of commercial uses; examples of which are shown in Table 1.1.[1, 2]

Table 1.1 – Uses of Various Linear α-Alkenes

Carbon Number	Use of α-Alkenes
C_4	Polyethylene co-monomer
C_6-C_8	Polyethylene co-monomer, plasticiser alcohol
C_{10}	Poly-α-alkene
C_{12}-C_{14}	Detergents
C_{16}-C_{18}	Drilling fluids, waxes, lubricant additives
C_{20+}	Lubricant additives

The largest production volume LAOs are 1-hexene and 1-octene, which are used as comonomers in the synthesis of linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) resins. 1-Hexene and 1-octene can also be used in the production of alkyl aromatics, alkyl silanes, metal alkyls and detergent alcohols. Research into this area has developed quickly due to these industrial applications.[1]

Chevron Phillips, Ineos and Shell use ethene oligomerisation for the large scale production of α-alkenes, two examples of these processes being the Shell Higher Olefin Process (SHOP), as shown in Scheme 1.1 and modifications of Ziegler's "Aufbau" process.[2, 3]



Scheme 1.1 – Shell Higher Olefin Process – Oligomerisation Stage

These methods produce a broad range of α-alkenes, known as a Schulz Flory distribution, resulting from an ethene insertion/β hydride elimination mechanism. A multi-stage reactor scheme can narrow this to a Poisson distribution; however a mixture of products is always obtained. Crucially the market demand of each α-alkene behaves differently in terms of market size, growth, fragmentation and technical services. However the range of α-alkenes produced does not correspond with market demand and the separation of α-alkenes from these compounds is costly. This provides industry with a challenge to find more selective catalytic systems which can be used to synthesise specific α-alkenes on demand.[1, 4, 5]

Extensive research has taken place to find catalysts that can selectively trimerise or tetramerise ethene to 1-hexene or 1-octene. The selectivity of these methods means that a different mechanism to the insertion/elimination mechanism is needed to produce the desired alkenes.

1.2. Ethene Trimerisation

Ethene trimerisation is a method of selectively synthesising 1-hexene and a high percentage of research into selectively forming α-alkenes is focused on this area. An attraction is that this method is 100 % 'atom efficient', as shown in Scheme 1.2.[2]

Scheme 1.2 – Ethene Trimerisation

Ethene trimerisation was first discovered by Manyik and co-workers at Union Carbide Corporation in 1967.[6] Manyik observed that while using Cr(III) 2-ethylhexanoate as the catalyst and partially hydrolysed tri-isobutyl aluminium (P*i*BAO) as the activator (co-catalyst) to polymerise ethene, the polymer produced contained butyl side chains. An explanation for this observation is the production of 1-hexene followed by incorporation of 1-hexene into the polymer chain. This was verified by further work in 1977, in which the group found a range of α-alkenes, including 1-butene (1-C_4), 1-hexene (1-C_6), 1-octene (1-C_8) and 1-decene (1-C_{10}) were produced in the liquid phase of the polymerisation.[7] Further observation showed that the rate of 1-C_6 production had a greater dependence on temperature and pressure than the rate of polymerisation, with the rate of 1-hexene formation being a second order with relation to ethene pressure. This suggested that the formation of 1-hexene did not follow the common linear chain growth mechanism and actually followed another mechanism. This is discussed in Section 1.4. First, an overview of the different catalyst structures which are successful for this reaction will be discussed.

1.2.1. Chromium Catalysts

It has been shown that chromium based trimerisation catalysts generally show higher selectivity, activity and thermal stability compared to other metals, for example tantalum and titanium.[2] A wide range of ligands have been investigated, a selection of which are summarised in this section. Tables 1.2 to 1.6 give the overall selectivity to hexenes and the selectivity to 1-hexene within the C_6 fraction.

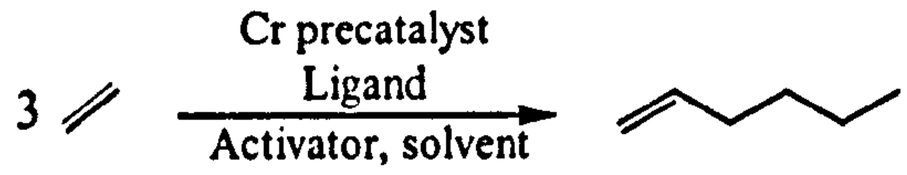
1.2.1.1. Aromatic Ligands

A chromium pyrrolyl catalyst developed by Chevron Phillips was the first catalyst to show 1-hexene selectivity of greater than 90 %.[2] A plant commercialising this technology was brought online in Qatar in 2003 and a high percentage of patents filed on ethene oligomerisation are based on this catalyst. A chromium pyrrolyl catalyst was chosen as chromium cyclopentadienyl complexes had previously been used as catalysts in ethene polymerisation and pyrrolyl ligands are heterocyclic analogues of cyclopentadienyl ligands.

Reagan investigated a range of chromium pyrrolyl complexes, such as the pentanuclear $[Cr_5(C_4H_4N)_{10}(C_4H_4O)_4]$ and the di-anionic complex $[Cr(C_4H_4N)_4]Na_2.(C_4H_4O)_2$; a number of these complexes exist as inorganic polymers.[8, 9] It was found that these complexes were active towards ethene oligomerisation under 30 bar of ethene at 90 °C when activated with 25 molar equivalents of triethylaluminium (TEA). The selectivity and activity of these catalysts depends on the catalyst precursor and the support with the best results coming from $[Cr_5(C_4H_4N)_{10}(C_4H_4O)_4]$ supported on Al_2O_3, giving an activity of 10,500 g (g Cr h)$^{-1}$, the products were made up of 31 % liquid oligomers. Using $\{[Cr(C_4H_4N)_2]Cl\}_n$ polymer as the precatalyst gave 99 % liquid oligomers with a selectivity of over 90 % to hexenes, of which 92 % was 1-hexene. This system only showed an activity of 1030 g (g Cr h)$^{-1}$ but proved that selectivities of over 80 % were obtainable.[9]

On improving this system Reagan found that the active catalyst could be prepared *in situ* without preforming the chromium pyrrolyl complex. [10, 11] This was carried out by mixing a chromium(III) alkanoate with pyrrole and TEA as the activator in cyclohexane. 2,5-Dimethylpyrrole was the ligand favoured by Phillips, since it showed good catalytic activity, with high thermal, light and air stability. In 1999, Phillips had developed a catalyst that provided activities of greater than 156,666 g/g Cr per hour at 100 °C and 100 bar with selectivities to C_6, of 93.8 % with an overall selectivity to 1-C_6, of 93 %. The catalyst was prepared by mixing Cr(III) 2-ethylhexanoate, 2,5-dimethylpyrrole, diethyl aluminium chloride (DEAC) and TEA in toluene at room temperature.[8]

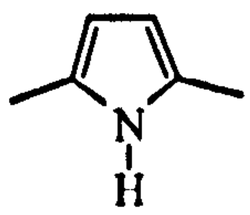
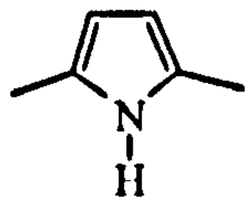
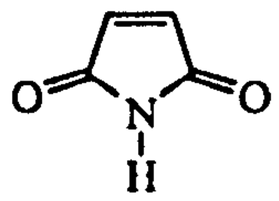
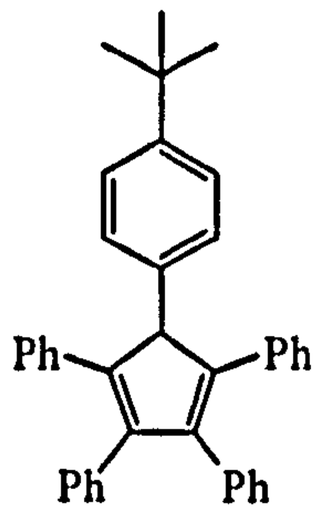
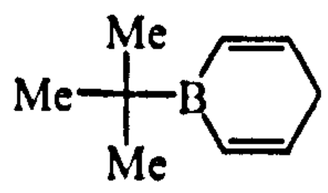
The success of the Phillip catalyst led to research into other ligands to use with a chromium precursor. Mitsubishi Chemical Corporation found that selectivities and activities were improved when a Lewis acid, such as $B(C_6F_5)_3$, was used.[12] This company also found that by preparing the Phillips catalyst *in situ* during a continuous trimerisation process, a productivity of 3,780,000 g (g Cr h)$^{-1}$ was achieved, with an overall 1-C_6 selectivity of 95.4 %, although this was only achieved with careful control of the molar ratios of 1-hexene to ethene in the reactor (reaction 1.1 in Table 1.2).[13] A large number of patents have been filed by other companies using variations on the Phillips catalyst, such as Sasol Technology and Sumitomo Chemical Company, although the productivities reported are not as high as that reported by Phillips or Mitsubishi.[8-15] Another aspect of the Phillips catalyst is that imidazolium-based ionic liquids, containing $[Al_nCl_nEt_{3n}]$ based anions, can be used as the solvent, as discovered by Sasol Technology.[16] An advantage of using ionic solvents is that the reaction is biphasic and so the alkene products can be easily separated and the catalyst regenerated. Using [1-ethyl-2,3-dimethylimidazolium][Al_nClEt_{3n}] (reaction 1.2 in Table 1.2) as the solvent, with Cr(III) 2-ethylhexanoate, 2,5-dimethylpyrrole and TEA at 115 °C and 50 bar of ethene, a productivity of 25,000 g (g Cr h)$^{-1}$ was achieved. This system gave selectivity to hexene of 75 % and 1-hexene (within C_6 fraction) of 87 %, giving an overall selectivity to 1-hexene of 65.3 %.



Scheme 1.3 – Ethene Trimerisation Reaction Scheme

Table 1.2 shows a list of catalytic systems with aromatic ligands, with the reaction scheme shown in Scheme 1.3.[2]

Table 1.2 – Catalytic Systems Used for Ethene Trimerisation with Aromatic Ligands

Reaction	Ligand	Chromium Precursor	Activator and Solvent	Conditions	Productivity, Selectivity
1.1		Cr(III) ethyl hexanoate	TEA C_2Cl_6	105 °C, 50 bar C_2H_4	945,000 g (g Cr h)$^{-1}$, C_6 – 95.9 % (1-C_6 - 95.4 %)
1.2		Cr(III) ethyl hexanoate	TEA, [1-ethyl-2,3-dimethyl-imidazolium] [$Al_nCl_nEt_{3n}$]	115 °C, 50 bar C_2H_4	25,000 g (g Cr h)$^{-1}$, C_6 – 87.0 % (1-C_6 – 65.3 %)
1.3		Cr(III) ethyl hexanoate	TEA, $AlClEt_2$	120 °C, 40 bar C_2H_4	278,000 g (g Cr h)$^{-1}$, C_6 – 93.2 % (1-C_6 – 79.6 %)
1.4		Cr(III) ethyl hexanoate	TEA C_2Cl_6	100 °C, 50 bar C_2H_4	57,700 g (g Cr h)$^{-1}$, C_6 – 93.5 % (1-C_6 – 77.2 %)
1.5		$[CrCl_3(thf)_3]$	TEA LDA	80 °C, 35 bar C_2H_4	1,072 g (g Cr h)$^{-1}$, C_6 – 85.8 % (1-C_6 – 62.5 %)

Reaction 1.3 in Table 1.2 shows an example of the use of malemide as a ligand for ethene trimerisation, developed by the Tosoh Corporation.[13] Using the reaction scheme and conditions indicated in reaction 1.3 in Table 1.2, productivities of up to 278,000 g (g Cr h)$^{-1}$ were obtained, with 98.5 % of the products being liquid oligomers. The system gave a selectivity to hexene of 93.2 % and an overall 1-hexene selectivity of 79.6 %. It was found that supporting the catalyst on SiO_2 improved performance but increased the amount of polyethylene produced.

Another class of ligands similar to the ligand used in the Phillips catalyst is cyclopentadienyl ligands. Sasol Technology found that having bulky aromatic substituents on the cyclopentadienyl ring switches the selectivity from polymerisation to

ethene trimerisation.[17] One of the best results seen is reaction 1.4 in Table 1.2, giving a productivity of 57,700 g (g Cr h)$^{-1}$, with a selectivity to hexene of 93.4 % and an overall selectivity to 1-hexene of 77.2 %. It was also found that the selectivity towards 1-hexene within the hexene fraction depended on the substituents of the cyclopentadienyl ring, systems with less bulky ligands had a lower selectivity to 1-hexene. Increasing the temperature in reaction 1.3 to 70 °C, increases the productivity to 93,500 g (g Cr h)$^{-1}$. Boratabenzenyl ligands are isoelectronic to cyclopentadienyl ligands and therefore were tested for ethene trimerisation by Mitsubishi Chemical Industries.[18] 1-Hexene was produced, with a selectivity of 62.5 % but the productivity was only 1072 g (g Cr h)$^{-1}$, as shown in reaction 1.5 in Table 1.2.

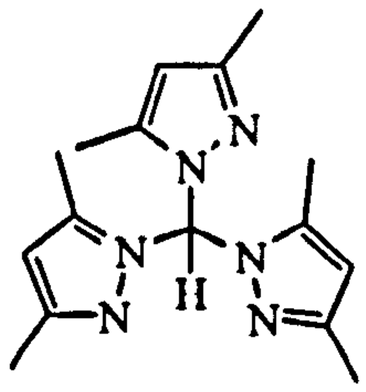
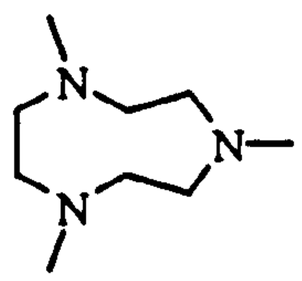
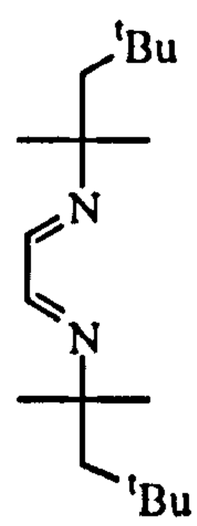
1.2.1.2. Multidentate Heteroatomic Ligands

Nitrogen Based Ligands

A number of chromium catalysts based on nitrogen donor ligands have been described; the performance of selected systems is shown in Table 1.3.

Reaction 1.6 in Table 1.3 shows a system using tris(pyrazolyl)methane ligands. The Tosoh Corporation tested these ligands for ethene trimerisation and found that these systems were active towards ethene trimerisation when activated with MAO or trialkyl aluminium.[19] Complexes were synthesised by reacting the ligand with $[CrCl_3(thf)_3]$ in tetrahydrofuran and the ligands coordinated facially to the metal. The four ligands investigated were tris(3,5-dimethyl-1-pyrazolyl)methane, tris(3-phenyl-5-methyl-1-pyrazolyl)methane, tris(3-phenyl-1-pyrazolyl)methane and tris(3-(4-tolyl)-1-pyrazolyl)-methane. These complexes were activated by either MAO or a mixture of MAO and Al(*n*-octyl)$_3$ or Al*i*Bu$_3$. The best results came from Reaction 1.6 in Table 1.3. This system gave a productivity of 40,100 g (g Cr h)$^{-1}$, the liquid fraction contained 0.1 % C_4, 99.6 % C_6, of which 99.5 % was 1-C_6 and 0.3 % C_8, with an overall selectivity to 1-hexene of 99.1 %.

Table 1.3 – Catalytic Systems Used for Ethene Trimerisation with Multidentate Nitrogen Ligands

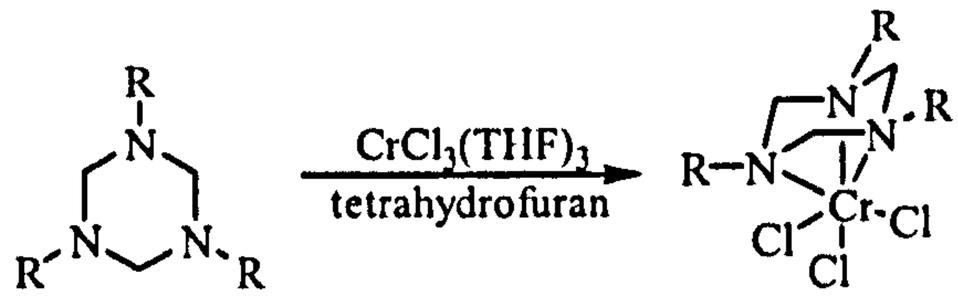
Reaction	Ligand	Chromium Precursor	Activator and Solvent	Conditions	Productivity, Selectivity
1.6		$[CrCl_3(thf)_3]$	MAO toluene	80 °C, 40 bar C_2H_4	40,100 g $(g\ Cr\ h)^{-1}$, C_6 – 99.6 % (1-C_6 – 99.5 %)
1.7		$[CrCl_3(thf)_3]$	NHAO[a] toluene	105 °C, 29 bar C_2H_4	12,309 g $(g\ Cr\ h)^{-1}$, C_6 – 39.3 % (1-C_6 – 37.3 %)
1.8		Cr(III) ethyl hexanoate	TEA, heptane	120 °C, 40 bar C_2H_4	22,995 g $(g\ Cr\ h)^{-1}$, C_6 – 72.4 % (1-C_6 – 58.3 %)

[a] NHAO is *n*-hexylaluminoxane

Wu and co-workers, as part of the Albermarle Corporation, filed a patent in which it was concluded that for nitrogen based ligands to be active and selective for ethene trimerisation, the ligands should be bulky.[20] A group of ligands believed to satisfy this criteria are 1,4,7-triazacycloalkane ligands. Wu describes a system comprising of chromium complexes of triazacyclononane, such as 1,4,7-trimethyl-1,4,7-trazacyclononane, as shown in reaction 1.7 in Table 1.3; it was suggested that these ligands would be able to promote trimerisation and oligomerisation and inhibit polymerisation. The ligand systems, which were pre-formed before testing, produced a Schultz Flory distribution of α-alkenes, with a high percentage of 1-hexene. The catalytic system in reaction 1.7 gave 9.4 % C_4, 39.3 % C_6, 10.0 % C_8, 8.5 % C_{10}, 6.9 % C_{12}, 6.0 % C_{14}, 5.0 % C_{16}, 4.0 % C_{18} and 10.9 % C_{20+}, with a selectivity to α-alkenes ranged between 85 to 95 % and a productivity of 12,309 g $(g\ Cr\ h)^{-1}$. Internal alkenes, cyclic alkenes and paraffins were also produced. It was calculated that if the system

produced a true Schultz Flory distribution, then the percentage of 1-hexene produced would be 10 %. The actual percentage produced was 39.3 %, suggesting the mechanism follows a metallacycle route as well as the linear chain growth route.[20]

Another group of tridentate nitrogen ligands have been investigated by Köhn and co-workers, known as triazacyclohexanes, as shown in Scheme 1.4.[21, 22]



Scheme 1.4 – Coordination of Triazacyclohexane Ligands to Chromium

Köhn found that upon activation with methylaluminoxane (MAO) or $[PhMe_2NH][B(C_6F_5)_4]/AliBu_3$ these catalysts were active for ethene polymerisation. Evidence of butyl side chains in the polyethylene polymer was seen in ^{13}C NMR spectroscopy, suggesting that 1-hexene is also produced in the reaction.[21] It was also found that it was possible to trimerise higher α-alkenes using these systems and this is explained further in Section 1.3.

Diimine ligands are well known in systems for ethene polymerisation and so were tested for ethene trimerisation.[2] Sumitomo Chemical Company filed a patent on this group of ligands for ethene trimerisation, using a system consisting of a chromium precursor, a diimine ligand (a general ligand shown in Figure 1.1) and an alkyl aluminium activator.[23]

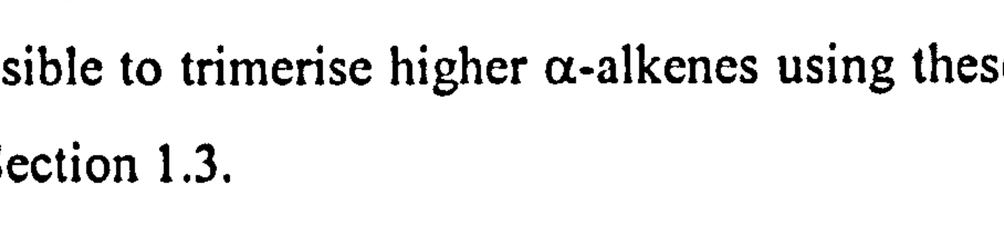
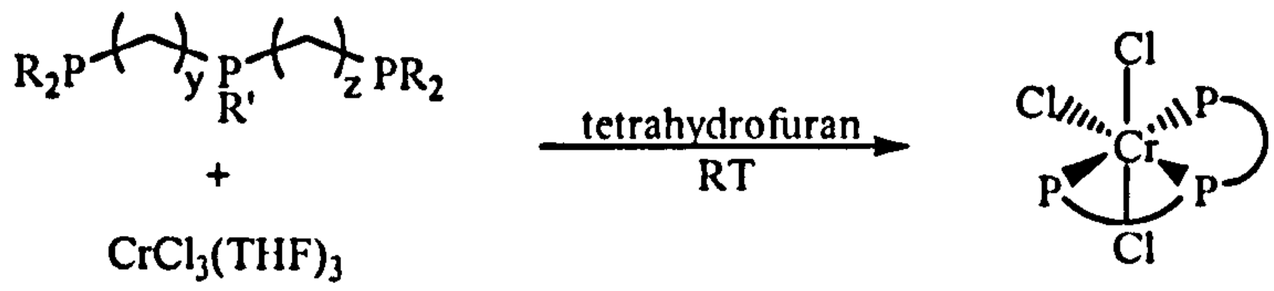


Figure 1.1 – General Structure of Diimine Ligands Tested by Sumitomo Chemical Company

One of the most active catalytic system that was tested is shown as reaction 1.8 in Table 1.3, with chromium(III) ethylhexanoate, glyoxalbis(1,1,3,3-tetramethylbutylimine) and TEA. At 120 °C and 40 bar of ethene, a productivity of 22,995 g (g Cr h)$^{-1}$ was achieved, the reaction mixture contained 12.2 % C_4, 72.4 % C_6, 1.5 % C_8, 9.4 % C_{10} and 3.0 % polyethylene. The selectivity to 1-C_6 within the C_6 fraction was 80.5 %, giving an overall selectivity of 58.3 %. Adding 15 molar equivalents of *n*-butylbromide can increase the overall selectivity to 1-C_6 to 79.8 %, although the productivity was reduced to 16,849 g (g Cr h)$^{-1}$.[23]

Phosphorus Based Ligands

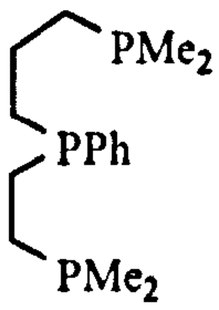
Ethene trimerisation systems comprising of polydentate phosphines were first developed by Amoco Corporation.[24] The general formula for the ligands tested is shown in Scheme 1.5.



Scheme 1.5 – General Phosphines Used by Amoco Corporation

Crystal structure determination of the chromium trichloride complexes of these ligands show a meridional coordination, a different arrangement compared to the triazacycloalkane and tris(pyrazolyl)methane ligands, which both adopt a facial arrangement.

Table 1.4 – Catalytic Systems Used for Ethene Trimerisation with Phosphorus Based Ligands

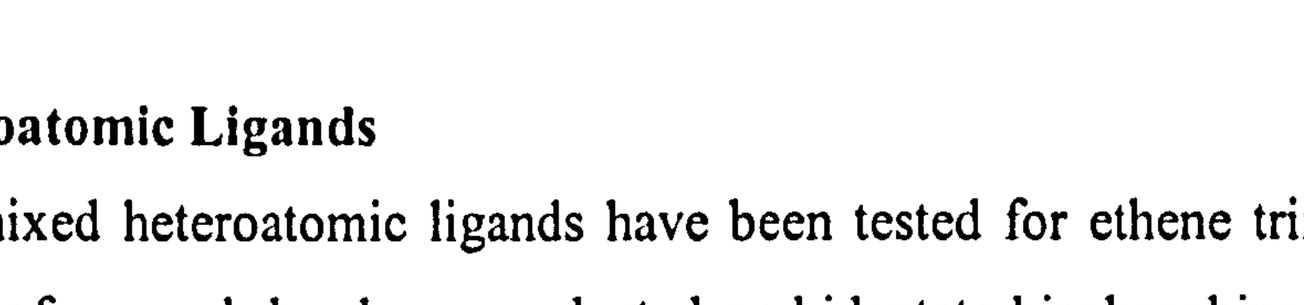
Reaction	Ligand	Chromium Precursor	Activator and Solvent	Conditions	Productivity, Selectivity
1.9		$[CrCl_3(thf)_3]$	BuAO toluene	80 °C, 40 bar C_2H_4	33,926 g (g Cr h)$^{-1}$, C_6 – 97.7 % (1-C_6 – 98.8 %)

Reaction 1.9 in Table 1.4 shows the system which gave the best results out of the ligands tested by Amoco Corporation.[24] $[CrCl_3(thf)_3]$, (2-dimethylphosphinoethyl)(3-dimethyl-phosphinopropyl)phenylphosphine and butylaluminoxane (BuAO) gave a productivity of 33,926 g (g Cr h)$^{-1}$ at a temperature of 80 °C and 40 bar of ethene. The product mixture contained 1.0 % C_4, 97.7 % C_6, 1 % C_{10} materials and 0.3 % polyethylene. The selectivity to 1-hexene within the C_6 fraction was 98.8 % and 96.5 % overall. In this system the precatalyst was formed before activation because it was found that having a three component system lowered the productivity and increase the percentage of polymer formed to about 12 %.

Mixed Heteroatomic Ligands

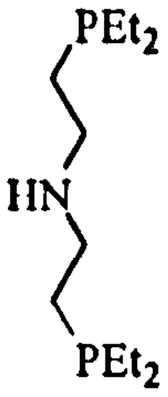
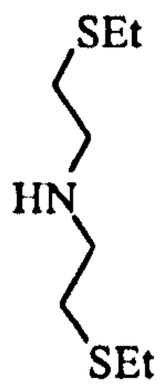
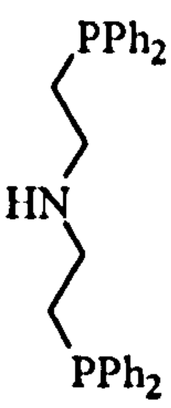
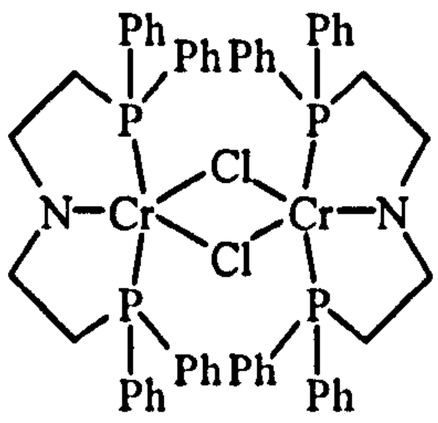
A range of mixed heteroatomic ligands have been tested for ethene trimerisation. A large amount of research has been conducted on bidentate bisphosphinoamine ligands, these ligands are explained in Section 1.2.1.3. Table 1.5 shows a selection of mixed heteroatomic systems.

Sasol Technology have investigated tridentate bisphosphinoamine ligands with the formula $R_2PCH_2CH_2NHCH_2CH_2PR_2$, as shown in Scheme 1.6.[25]



Scheme 1.6 - Tridentate Bisphosphinoamine Ligands

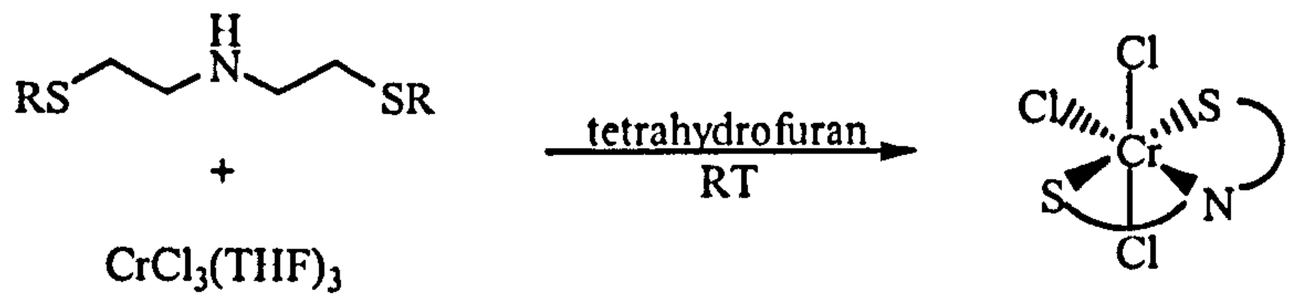
Table 1.5 – Catalytic Systems Used for Ethene Trimerisation with Multidentate Mixed Heteroatomic Ligands

Reaction	Ligand	Chromium Precursor	Activator and Solvent	Conditions	Productivity, Selectivity
1.10		$[CrCl_3(thf)_3]$	MAO (850 eq)	100 °C, 40 bar C_2H_4	37,400 g (g Cr h)$^{-1}$, C_6 – 94.0 % (1-C_6 – 99.1 %)
1.11		$[CrCl_3(thf)_3]$	MAO (280 eq)	90 °C, 30 bar C_2H_4	160,840 g (g Cr h)$^{-1}$, C_6 – 98.4 % (1-C_6 – 98.1 %)
1.12		$[CrCl_3(thf)_3]$	MAO (300 eq)	80 °C, 40 bar C_2H_4	13,284 g (g Cr h)$^{-1}$, C_6 – 98.7 % 1-C_6 – 98.4 %
1.13			MAO (300 eq)	80 °C, 40 bar C_2H_4	7,800 g (g Cr h)$^{-1}$, C_6 – 79.8 % 1-C_6 – 78.3 %

The complexes shown in Scheme 1.6 are formed by reacting the ligand with $[CrCl_3(thf)_3]$ at room temperature in tetrahydrofuran. Crystal structure determination showed the ligands bonded by a meridional coordination of the ligand, with a distorted octahedral geometry. Highly active ethene trimerisation catalysts were formed on activation with MAO, with a high selectivity towards 1-hexene. Using $[Cr(Et_2PCH_2CH_2NHCH_2CH_2PEt_2)Cl_3]$ (reaction 1.10 in Table 1.5), 850 molar equivalents of MAO, at 100 °C and 40 bar of ethene, a productivity of 37,400 g (g Cr h)$^{-1}$ was obtained. The product mixture consisted of 94 % C_6, of which 99.1 % was 1-C_6, giving an overall selectivity to 1-C_6 of 93.2 %. The mixture also

contained 2.1 % polyethylene. Selectivity and activity is affected by the steric bulk of the R group where high activity and selectivity is produced if the R group is a small alkyl group. Investigations into the optimisation of reaction conditions showed that the catalyst has a higher stability at 80 °C than 100 °C and deactivation occurs over longer run times.

Sasol Technology developed an alternative system to the tridentate bisphosphinoamine ligands using bis-sulphanylamine ligands, as shown in Scheme 1.7.[26-28] As with the bisphosphinoamine analogues, the bis-sulphanylamine ligand bonds to the chromium centre *via* a meridional arrangement and in comparison the bite angles of both tridentate bis-sulphanylamine and bisphosphinoamine ligands are very similar.



Scheme 1.7 - Tridentate Bis-sulphanylamine Ligands

Initial investigations were targeting ligands with sterically undemanding R groups, since these produced the best results for the bisphosphinoamine analogues. The complexes were synthesised using the same method as the bisphosphinoamine analogues, in tetrahydrofuran at room temperature. $[CrCl_3(EtSCH_2CH_2NHCH_2CH_2SEt)]$, activated with 280 molar equivalents of MAO, at 90 °C under 30 bar of ethene (reaction 1.11 in Table 1.5), gave a productivity of 160,840 g (g Cr h)$^{-1}$, with the products consisting of 98.4 % C_6, of which 99.7 % was 1-hexene and 0.16 % polyethylene. Ligand systems with substituents on the nitrogen other than hydrogen result in a significant decrease in activity and percentage of polyethylene produced can increase to over 60 % in certain cases. The hydrogen on the nitrogen may undergo deprotonation during activation to give an anionic amide ligand, suggesting this is important for high activity.[29]

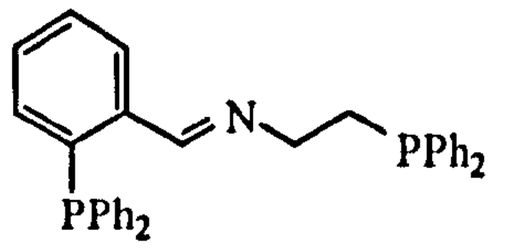
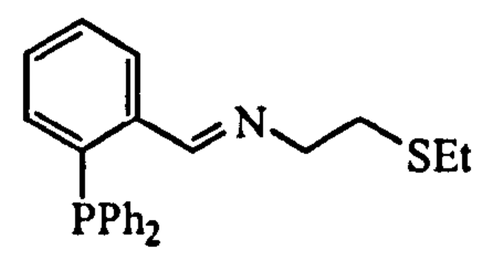
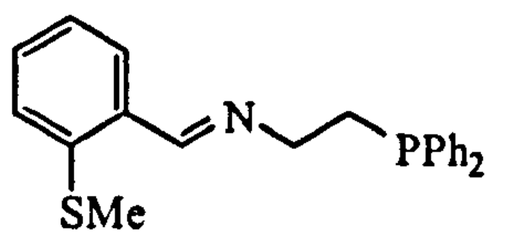
Ethene trimerisation was carried out using a range of ligands with Cr(III) and Cr(II) species, in order to investigate the oxidation state of chromium in the metallacycle mechanism. Reactions 1.12 and 1.13 in Table 1.5 shows two similar ligand systems

tested, reaction 1.12 uses $[CrCl_3(thf)_3]$ and reaction 1.13 uses $[CrCl_2(thf)_3]$, both systems use $Ph_2PCH_2CH_2NHCH_2CH_2PPh_2$ and are activated with MAO. As can be seen the two systems show similar productivities but the selectivity towards the C_6 fraction is lower in the Cr(II) system.[30]

An example of an Cr(II) dimer is shown as reaction 1.13 in Table 1.5, on activation with MAO this system gave a productivity of 7,800 g (g Cr h)$^{-1}$, with a selectivity to C_6 of 79.8 % and 2.2 % polyethylene, the overall selectivity to 1-hexene was 78 %.[30] If $t Bu_2SCH_2CH_2NHCH_2CH_2St Bu_2$, is used, the nitrogen acts as the bridging ligand and the percentage of polyethylene produced in trimerisation increases to 51.0 %. Activation with $AlR_3/B(C_6F_5)_3$ produced active trimerisation catalysts, with the amount added having a significant effect on activity, only 10 – 40 molar equivalents of activator was needed. Using $AlMe_3/B(C_6F_5)_3$ as the activator in reaction 1.12 in Table 1.5, with 10 molar equivalent of $AlMe_3$ gave 99.6 % C_6, with an overall 1-hexene selectivity of 99.2 % and a productivity of 11,656 g (g Cr h)$^{-1}$. It is thought that these ligands are deprotonated, being mono-anionic in the active species.

Temple and co-workers isolated the dimer $[Cr(\mu\text{-}Cl)Et(CySCH_2CH_2NCH_2CH_2SCy)][AlEtCl_3]_2$ by reacting $CrCl_3(CySCH_2CH_2NCH_2CH_2SCy)$ with $AlEt_2Cl$, where Cy is cyclohexyl.[31] The group found that the Cr(II) species $[Cr(ClAlEtCl_2)(CySCH_2CH_2NCH_2CH_2SCy)][AlEtCl_3]$ gave a productivity of 2,265 g (g Cr h)$^{-1}$ whereas the Cr(III) species $[Cr(\mu\text{-}Cl)Et(CySCH_2CH_2NCH_2CH_2SCy)][AlCl_3Et]_2$ gave a productivity of 9,383 g (g Cr h)$^{-1}$, therefore the Cr(III) oxidation state produces a more active trimerisation catalyst than the Cr(II) oxidation state. The alkyl aluminium activator can also reoxidise the Cr(II) species to Cr(III) and so if the catalyst is reduced to the less active Cr(II) species during the mechanism, the active Cr(III) species may be restored by reoxidation by the alkyl aluminium activator. The mechanism by which the Cr(II) is activated will be discussed in Section 1.4.3.3.[31]

Table 1.6 – Catalytic Systems Used for Ethene Trimerisation with Mixed PNP and PNS Imine Ligands

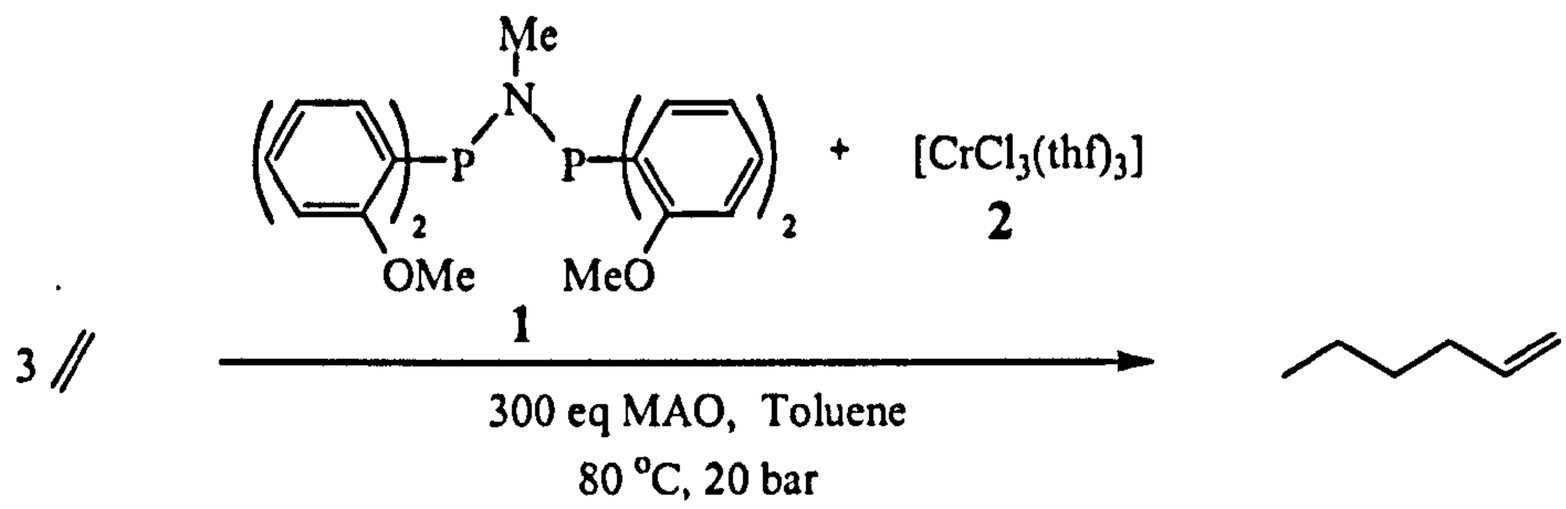
Reaction	Ligand	Chromium Precursor	Activator and Solvent	Conditions	Productivity, Selectivity
1.14		$[CrCl_3(thf)_3]$	MAO (100 eq)	24-30 °C, 30 bar C_2H_4	3,092 g (g Cr h)$^{-1}$, C_6 – 83.0 % (1-C_6 – 98.0 %)
1.15		$[CrCl_3(thf)_3]$	MAO (100 eq)	24-30 °C, 30 bar C_2H_4	1,223 g (g Cr h)$^{-1}$, C_6 – 82.0 % (1-C_6 – 98.0 %)
1.16		$[CrCl_3(thf)_3]$	MAO (100 eq)	24-30 °C, 30 bar C_2H_4	4521 g (g Cr h)$^{-1}$, C_6 – 10.0 %

Bluhm and co-workers tested mixed heteroatomic imines for ethene trimerisation, as shown in Table 1.6. [32] Upon activation with 100 molar equivalents of MAO, at about 30 °C, under 30 bar of ethene, the system in reaction 1.14 in Table 1.6 gave a productivity of 3,092 g (g Cr h)$^{-1}$, with a selectivity to C_6 fraction of 83.0 % and an overall selectivity 81.3 %. Reaction 1.15 in Table 1.6 shows a similar imine system, which has a similar selectivity to reaction 1.14 but lower productivity. The donor heteroatom in the ligand has a significant influence on determining whether the system is selective towards ethene trimerisation or polymerisation, this can be seen in reaction 1.16, Table 1.6, where the system has a selectivity to C_6 of only 10 % and 90 % polyethylene.

1.2.1.3. *N,N*-Bis(diphenylphosphino)alkylamine (PNP) Ligands

Previously palladium complexes of *N,N*-bis(diarylphosphino)alkylamine (PNP) ligands have been used in the copolymerisation of CO/ethene to give polyketones[33] and nickel complexes had been developed for ethene polymerisaton.[34, 35] It was subsequently found that these ligands were also highly active and selective towards ethene trimerisation, over the past few years, a significant amount of industrial and academic research has been conducted in this area. British Petroleum patented the first system

based on bidentate PNP ligands with the formula $Ar_2PN(R)PAr_2$, which when activated with MAO, gave a highly active trimerisation catalyst. This patent included one of the best systems reported, which is shown in Scheme 1.8, using *N,N*-bis(di-*ortho*-methoxyphenylphosphino)methylamine, **1**.[1, 4, 36, 37, 38]



Scheme 1.8 – Method for Trimerisation of Ethene with PNP Ligands

Trimerisation occurs *via* a 'one pot' process, by the reaction of a chromium precursor, $[CrCl_3(thf)_3]$ with the **1** ligand and MAO in toluene under an ethene atmosphere, the catalyst precursor is not preformed.[4] Upon activation with 300 equivalents of MAO, at 80 °C and under 20 bar of ethene, the catalyst system gave a productivity of 1,033,200 g (g Cr h)$^{-1}$, which was unprecedented for ethene trimerisation. The products consisted of 90 % C_6, 1.8 % C_8, 8.5 % C_{10} and no polyethylene. The selectivity to 1-hexene within the C_6 fraction is 99.9 %, giving an overall selectivity to 1-hexene of 89.9 %, see reaction 1.17 in Table 1.7. This catalyst is extremely active and under the same conditions the productivity is two orders of magnitude higher than other systems reported. Although the 1-hexene selectivity is not a high as other systems reported, this is largely a function of the batch reactor conditions, the high concentration of 1-hexene leading to significant re-insertion of 1-hexene and therefore increasing the amount of C_{10} and C_{14} materials present. The molecular structure of the precatalyst, $[CrCl_3(\mathbf{1})]$ is shown in Figure 1.2.[3, 39]

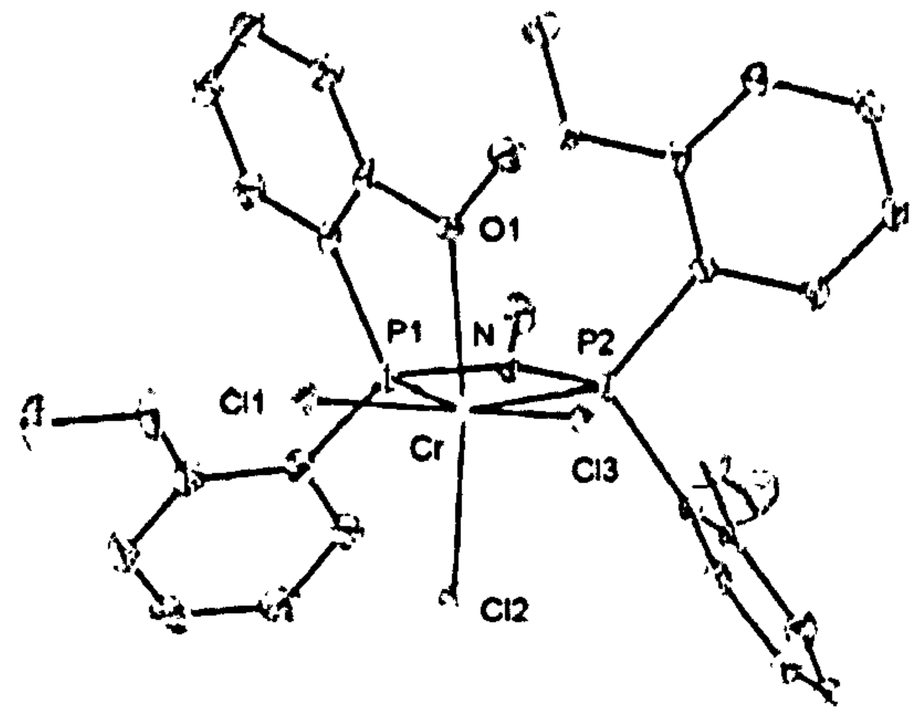
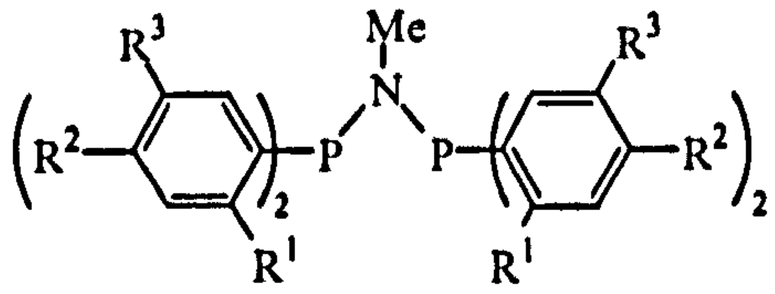


Figure 1.2 – Molecular Structure of [$CrCl_3$(1)][5]

The molecular structure reveals an octahedral arrangement of ligands around the chromium centre.[5] Ligand **1** coordinates to the chromium centre *via* two phosphorus atoms. The nitrogen atom does not bind to the metal centre but it is possible that the electronic properties of the chromium centre are affected by delocalisation of charge onto the nitrogen. It can be seen that an OMe group, on the *ortho* position of a aryl group, acts as a pendant ligand to create a tridentate system, which may stabilised the system during the catalytic cycle.

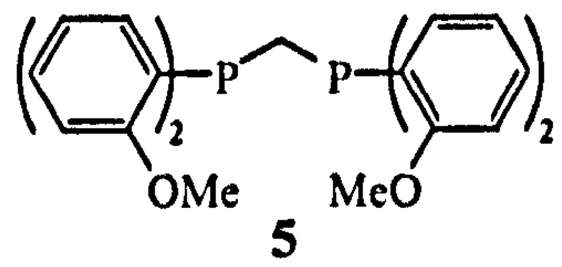
The system was shown to be active and selective at low ethene pressures and low temperatures.[4] At 1 bar of ethene and room temperature, without temperature control, a productivity of 8900 g (g Cr h)$^{-1}$ was achieved, with a selectivity to C_6 of 82.2 %, giving an overall selectivity to 1-hexene of 81.6 %, this is reaction 1.18 in Table 1.7. Figure 1.3 shows a selection of PNP ligands tested, with the results in Table 1.5.



1 - R^1=MeO, R^2=R^3=H

3 - R^1=Et, R^2=R^3=H

4 - R^1=R^3=H, R^2=OMe



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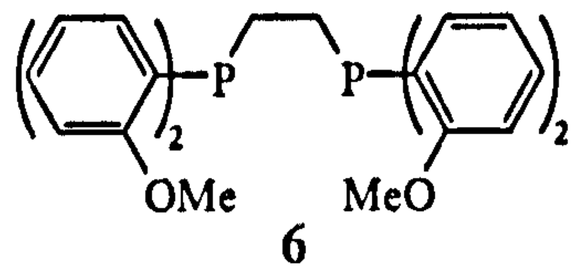


6

Figure 1.3 – Ligands Tested by Wass and Co-workers

Table 1.7 – Ligands Tested by Wass and Co-workers

Reaction	Ligand	Ethene Pressure / bar	Temperature / °C	Productivity / g (g Cr h)$^{-1}$	Selectivity (wt %)			
					C_6	1-C_6[b]	C_8	C_{10+}
1.17	1	20	80	1,033,200	90.0	89.9	1.8	8.5
1.18	1	1	RT	8,900	82.2	81.9	1.0	14.4
1.19[a]	3	1	RT	0	-	-	-	-
1.20[a]	4	1	RT	0	-	-	-	-
1.21[a]	5	1	RT	0	-	-	-	-
1.22[a]	6	1	RT	0	-	-	-	-

0.02 mmol [$CrCl_3(thf)_3$]. 0.02 mmol PNP ligand, 300 eq MAO, toluene diluent, 1h; [a] Modified MAO (MMAO) used as activator; [b] overall selectivity to 1-C_6.

It was found that steric bulk on the *ortho* position of the phenyl rings was responsible for the high activity of the system at low pressures. Referring to Figure 1.3, ligand **3** (reaction 1.19 in Table 1.7) with an ethyl group in the *ortho* position (R^1), which is sterically equivalent to a methoxy group, was inactive towards trimerisation under 1 bar of ethene and at room temperature. Ligand **4** (reaction 1.20 in Table 1.7), which is electronically the same as ligand **1**, was inactive under the same conditions. It was concluded that the reason for the high activity was the *ortho* pendant OMe group, which lead to the testing of ligands **5** and **6**, which were found to be inactive (reaction 1.21 and 1.22 in Table 1.7). This suggests that a combination of the nitrogen backbone and the

OMe group is required under these conditions. There is a second order dependence of catalyst activity on ethene pressure.

Bercaw and co-workers. synthesised a well defined version of this catalyst and this system was used to further understand the mechanism and activation of the catalyst (see sections 1.2.3 and 1.2.4).[5, 40] $[CrPh_3(\mathbf{1})]$, **7**, was synthesised as a model for the proposed $[CrMe_3(\mathbf{1})]$ intermediate in the formation of the active catalyst in Scheme 1.8, the molecular structure is shown in Figure 1.4. The molecular structure showed that again the OMe group acts as a pendant donor group. On activation with $[H(OEt_2)_2][B(C_6H_3(CF_3)_2)_4]$, in toluene, this system gives productivities comparable to the $[CrCl_3(thf)_3]$/**1**/MAO system.

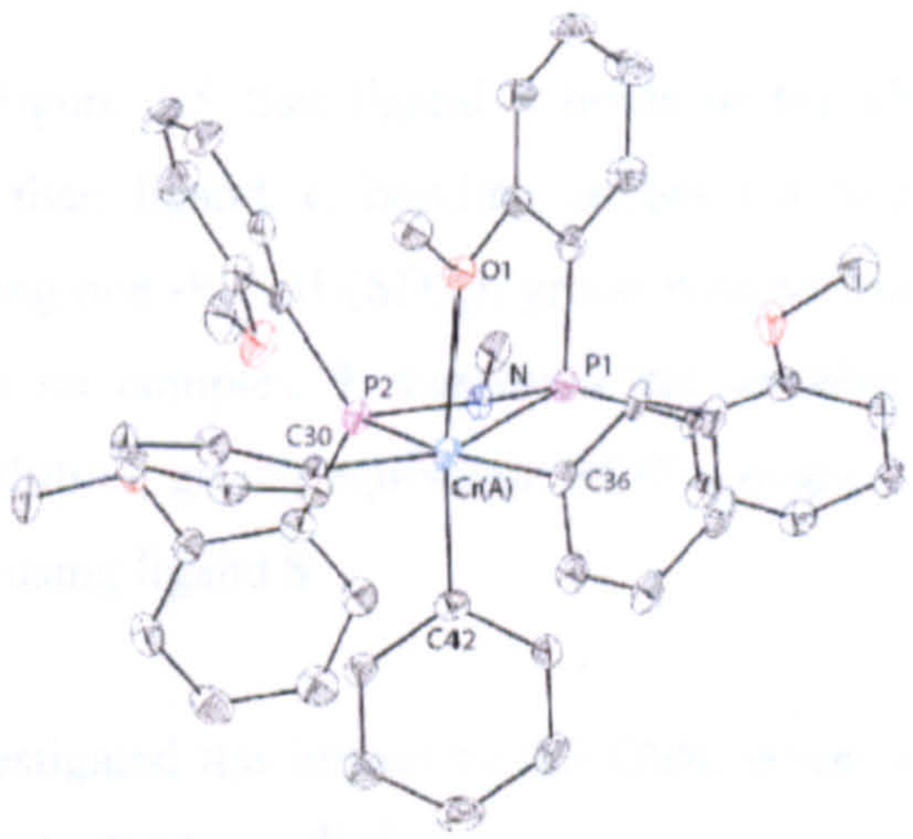
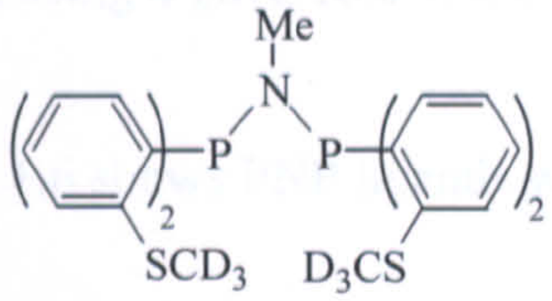


Figure 1.4 – Molecular Structure of $[CrPh_3(1)]$, 7[40]

Further studies into other functional groups that may act as a pendant donor lead to the synthesis of a PNP ligand with SCD_3 groups instead of OMe, ligand **7**.[40]



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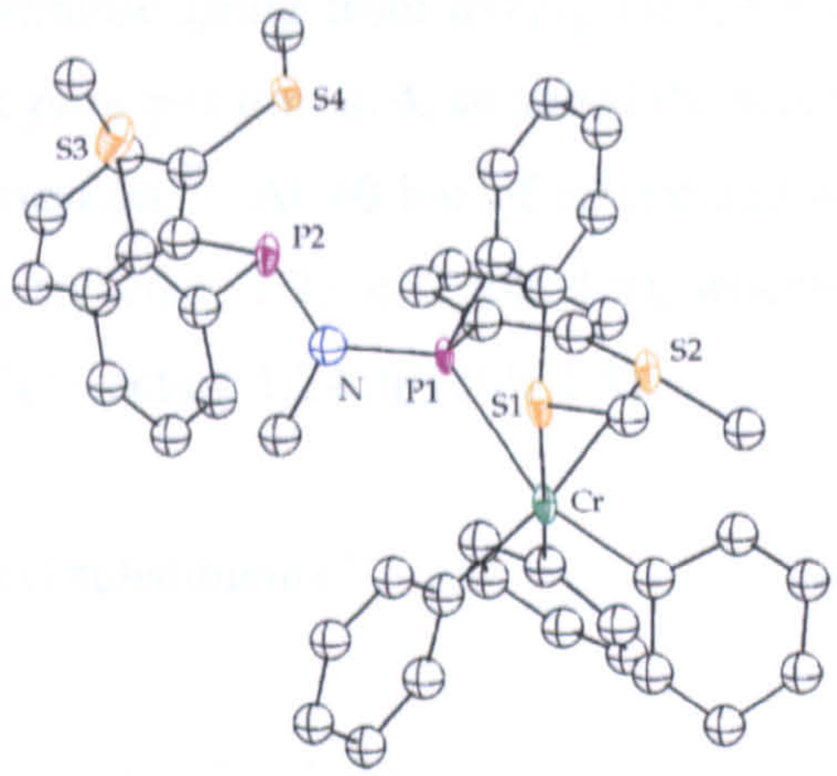


9

Figure 1.5 – Molecular Structure of [$CrPh_3$(8)], 9

It can be seen from Figure 1.5 that ligand **8** binds to the chromium centre with a different coordination than ligand **1**, bonding occurs *via* two sulphur atoms and a phosphorus atom, leaving one -$P(C_6H_5(SD_3))_2$ group with no interaction with the metal. ^2H NMR spectroscopy on complex **9**, suggested the complex undergoes a dynamic exchange process in solution, giving equivalent SCD_3 groups. There was no evidence of ethene trimerisation using ligand **8**.

Sasol Technology investigated the impact of the OMe group in more detail at higher ethene pressures, shown in Table 1.8.[41, 42]

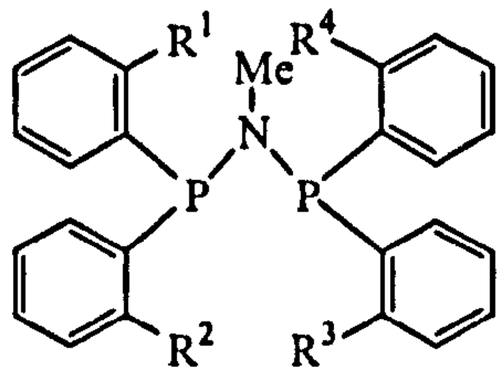
Table 1.8 – Catalytic Data from PNP Ligands with Ortho-Alkyl Substituents

Reaction	Ligand	Productivity / g (g Cr h)$^{-1}$	Selectivity (wt %)				
			C_6	1-C_6[a]	C_8	C_{10+}	PE
1.23	**1**	159,000	82.0	>99.0	13.0	17.0	<1.0
1.24	**4**	25,400	17.0	35.0	38.0	33.0	12.0

Standard conditions – 0.02 mmol [$Cr(acac)_3$], 0.04 mmol PNP ligand, 300 eq MAO, 100 mL toluene, 45 bar ethene, 45 °C, 10 mins run time; [a] overall selectivity to 1-C_6.

It was found that at high pressure and temperature going from having the OMe in the *ortho* position of the phenyl group in **1** to the *para* position in **4**, switched the selectivity of the system from trimerisation to tetramerisation.[42] At 40 bar of ethene and 45 °C, ligand **1** gave a selectivity to C_6 of 82.0 % (reaction 1.23 in Table 1.8), whereas the system using **4** gave 16.0 % C_6 and 38.0 % C_8 (reaction 1.24 in Table 1.8).

Figure 1.6 shows PNP ligands with *ortho*-alkyl substituents.[41]



3 - $R^1=R^2=R^3=R^4=Et$
10 - $R^1=R^2=R^3=R^4=Me$
11 - $R^1=R^2=R^3=R^4=iPr$
12 - $R^1=R^2=H$, $R^3=R^4=Me$

Figure 1.6 – PNP Ligands with Ortho-Alkyl Substituents

Table 1.9 – Catalytic Data from PNP Ligands in Figure 1.6

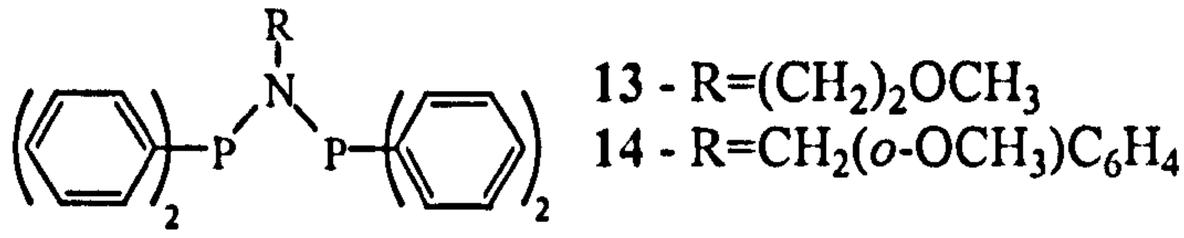
Reaction	Ligand	Productivity / g (g Cr h)$^{-1}$	Selectivity (wt %)				
			C_6	1-C_6[a]	C_8	C_{10+}	PE
1.25[b]	**3**	324,110	90.7	90.4	4.2	1.5	3.4
1.26[b]	**10**	298,800	86.0	85.2	10.5	0.3	3.3
1.27[c]	**11**	100,840	92.9	92.2	2.7	1.4	2.4
1.28[d]	**12**	37,470	17.1	9.5	66.0	1.4	8.3

Standard conditions – 0.033 mmol [$Cr(acac)_3$], 0.066 mmol PNP ligand, 300 eq MAO, 100 mL toluene, 45 bar ethene, 45 °C; [a] overall selectivity to 1-C_6; [b] 0.02 mmol [$Cr(acac)_3$], 10 mins run time; [c] 20 mins run time; [d] 18 mins run time.

The catalysts were prepared using a method adapted from work by Wass and co-workers by stirring the chromium precursor and the ligand in a solvent, then adding to a reactor containing the solvent and MAO.[4] Wass and co-workers showed that ligand **3** was inactive for trimerisation at low pressure but the system is active at higher ethene pressures (reaction 1.25 in Table 1.9), giving a productivity of 324,110 g (g Cr h)$^{-1}$, with

a selectivity to C_6 of 90.7 % and to 1-hexene of 99.7 % within C_6 fraction, which is an overall selectivity of 90.4 % to 1-hexene.[4, 41] Ligand **10** (reaction 1.26 in Table 1.9) has methyl groups in the *ortho* position, R, and produced a productivity of 298,800 g (g Cr h)$^{-1}$, with a lower selectivity to 1-hexene than ligand **3**. Having an isopropyl group in the R position (ligand **11**, reaction 1.27 in Table 1.9) reduces the productivity by a factor of two and having just two methyl group on the ligand (ligand **12**, reaction 1.28 in Table 1.9) switches the selectivity to the tetramerisation of ethene and reduces the productivity.[41] It is important in note that in these cases a high pressure is needed for 1-hexene or 1-octene production and that small changes to the substituents on the aryl ring can switch the selectivity from ethene trimerisation to ethene tetramerisation, this is explained in more detail in Section 1.4.

Bercaw and co-workers investigated PNP ligands with a range of ether donor groups on the nitrogen.[43] The donor groups on the backbone may act as pendant donors similar to the OMe on ligand **1**. The examples are shown in Figure 1.7.



13 - R=$(CH_2)_2OCH_3$
14 - R=$CH_2(o\text{-}OCH_3)C_6H_4$

Figure 1.7 – PNP Ligands with Ether Donor Groups on Nitrogen

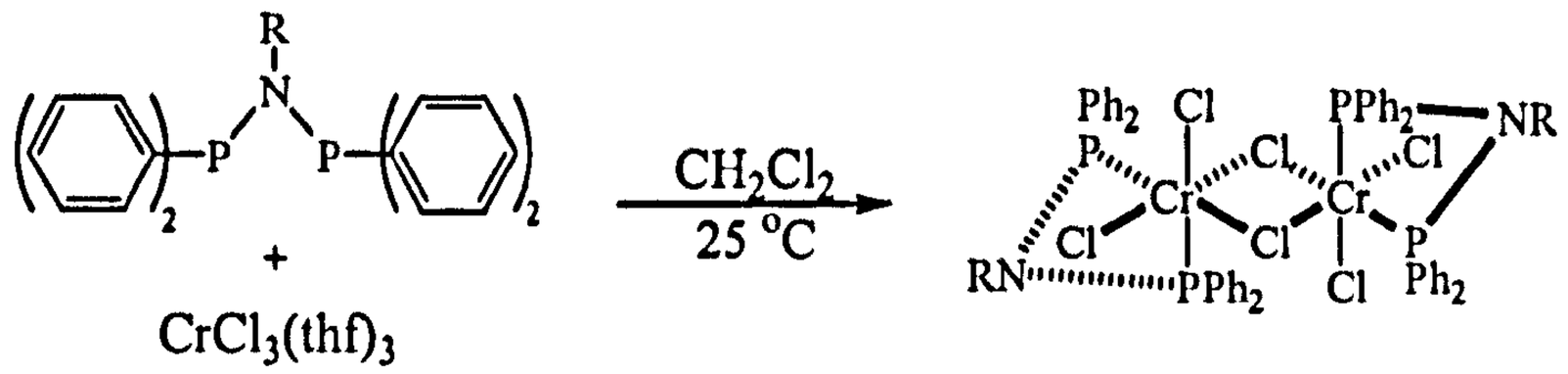
Table 1.10 shows the results obtained from the ligands in Figure 1.7.

Table 1.10 – Ethene Trimerisation with Ligands in Figure 1.7

Reaction	Ligand	Productivity / g (g Cr h)$^{-1}$	Selectivity (wt %)				
			C_6	1-C_6[a]	C_8	C_{10+}	PE
1.29	**13**	361	61.0	50.6	31.0	1.0	6.0
1.30	**14**	1625	62.0	57.7	24.0	7.0	<0.1

0.02 mmol $[CrCl_2(P,P\text{-}\kappa^2\text{-}(Ligand)(\mu_2\text{-}Cl)]_2$, 50 mL ClC_6H_5, 300 eq MAO, 1 atm ethene, 25 °C; [a] overall selectivity to 1-C_6.

The precatalyst was preformed giving a chromium dimer species as shown in Scheme 1.9.[43]



13 - R=$(CH_2)_2OCH_3$
14 - R=$CH_2(o\text{-}OCH_3)C_6H_4$

15 - R=$(CH_2)_2OCH_3$
16 - R=$CH_2(o\text{-}OCH_3)C_6H_4$

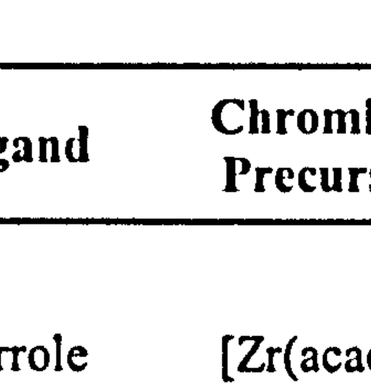
Scheme 1.9 – Complex Formation for Ligands $Ph_2PN((CH_2)_2OCH_3)PPh_2$, 13 and $Ph_2PN(CH_2(o\text{-}OCH_3)C_6H_4)PPh_2$, 14

The best results came from ligand **14** (run 1.30 in Table 1.10), where R=$CH_2(o\text{-}OCH_3)C_6H_4$. On forming complex **16** in Scheme 1.9, followed by activation with MAO, a productivity of 1625 g (g Cr h)$^{-1}$ was achieved, with a selectivity to C_6 of 62 %, to C_8 of 24 % and an overall selectivity of 1-hexene of 57.7 %. C_{10} and C_{12} materials were detected from incorporation of C_6 and C_8 materials into the mechanism. The molecular structure of complex **15** shows that the donor group on the nitrogen does not act as a pendant ligand and the productivity of the catalyst is 361 g (g Cr h)$^{-1}$ (reaction 1.29 in Table 1.10) compared to over a million g (g Cr h)$^{-1}$ for the $[CrCl_3(thf)_3]$/**1** system.[4] Other bidentate PNP ligands are described in Section 1.4.1, as these systems can also tetramerise ethene to 1-octene.

1.2.2. Non-Chromium Trimerisation Catalysts

Zirconium,[8] vanadium,[8] tantalum[44] and titanium[8, 45, 46] trimerisation catalysts have been developed. A selection of these catalysts is highlighted in Table 1.11.

Table 1.11 – Non-chromium Trimerisation Catalysts

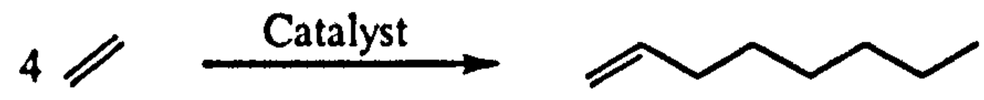
Reaction	Ligand	Chromium Precursor	Activator and Solvent	Conditions	Productivity, Selectivity[a]
1.31[b]	Pyrrole	$[Zr(acac)_2]$	TEA cyclohexane	80 °C, 38 bar C_2H_4	29 g(g Zr h)$^{-1}$, C_6 – 26.9 % 1-C_6 – 26.9 %
1.32[b]	Pyrrole	$[V(O)(acac)_2]$	TEA cyclohexane	80 °C, 38 bar C_2H_4	115 g(g V h)$^{-1}$, C_6 – 63.0 % 1-C_6 – 50.0 %
1.33[c]	'naked' catalyst	$[TaCl_5]$	$[Zn(CH_3)_2]$ ClC_6H_6	45 °C, 48 bar C_2H_4	214 g(g Ta h)$^{-1}$, C_6 – 98.7 % 1-C_6 – 97.1 %
1.34[d]			MAO (1000 eq)	30 °C, 2 bar C_2H_4	22,354 g(g Ti h)$^{-1}$, C_6 – 87 % 1-C_6 – 98 %

[a] selectivity to 1-C_6 is overall selectivity; [b] reference 8, [c] reference 44, [d] reference 8, 45, 46.

In contrast to the chromium systems, the non-chromium catalysts in Table 1.11 show low activity towards ethene trimerisation and low selectivity towards the C_6 fraction. In many cases the products consist of a high percentage of polyethylene. In reaction 1.33 in Table 1.11, $[Zn(CH_3)_2]$ is used as an alkylating agent to form $[TaCl_2(CH_3)_2]$.[44] Reaction 1.34 shows a titanium system developed by Hessen and co-workers.[8, 45, 46] This system was one of the first active and selective non-chromium trimerisation catalysts, giving a productivity of 22,354 g (g Ti h)$^{-1}$, with a selectivity to C_6 of 87 %, of which 98 % was 1-C_6. It was found that the phenyl group on the cyclopentadienyl ligand acts as a pendant ligand and is important for high activity.

1.3. Ethene Tetramerisation

Ethene tetramerisation is a method of selectively forming 1-octene from ethene, as shown in Scheme 1.10.

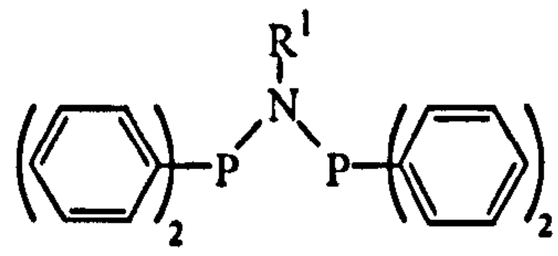


Scheme 1.10 – Ethene Tetramerisation

This reaction was first reported by Bollmann and co-workers in 2004.[47] Previous to this report it was believed that ethene tetramerisation was unlikely to occur.[48, 49] A series of chromium PNP systems have been shown to be active towards 1-octene formation, some examples are given within this section.

1.3.1. *N,N*-Bis(diphenylphosphino)alkylamine (PNP) Ligands

Bollmann and co-workers reported an ethene tetramerisation catalyst using $[CrCl_3(thf)_3]$, PNP ligands and MAO as an activator. A range of PNP ligands were tested, with various substituents on both the phosphorus and nitrogen atoms. Selectivities towards 1-octene of up to 70 % was achieved, 1-hexene, methylcyclopentane and methylene cyclopentene were the major side products.[42, 47] Figure 1.8 shows PNP ligands with alkyl substituents on the nitrogen and the ethene tetramerisation results are shown in Table 1.12.



17 - R^1=Me
18 - R^1=Cyclohexyl
19 - R^1=*i*Pr

Figure 1.8 – PNP Ligands Tested by Bollmann and Co-workers for Ethene Trimerisation

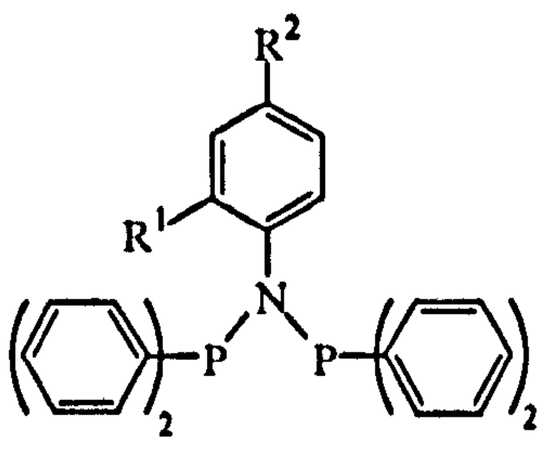
Table 1.12 – Ethene Tetramerisation with Ligand in Figure 1.8

Reaction	Ligand	Time / mins	Productivity / g (g Cr h)$^{-1}$	Selectivity (wt %)				
				C_6	1-C_6[a]	C_8	1-C_8[b]	PE
1.35	**17**	30	26,500	24.8	39.4	59.0	94.1	1.4
1.36	**18**	30	8,050	32.1	86.1	59.4	99.3	0.5
1.37[c]	**19**	30	272,400	16.9	70.3	68.3	98.9	1.1

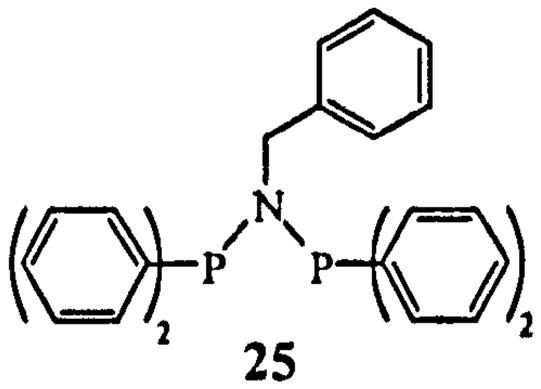
Standard conditions – 0.033 mmol [$CrCl_3(thf)_3$], 0.066 mmol PNP Ligand, 300 equivalents MAO, 100 mL toluene, 30 bar ethene, 60 °C; [a] selectivity to 1-C_6 within C_6 fraction; [b] Selectivity to 1-C_8 within C_8 fraction; [c] [$Cr(acac)_3$], 45 bar ethene, 45 °C.

It was reported that the substituent on the nitrogen has little effect on the selectivity to 1-octene within the C_8 fraction, although the productivity and selectivity to 1-hexene were affected, as seen in Table 1.12.[42, 47] The best results were produced by ligand **19**, reaction 1.37 in Table 1.12. At 45 bar of ethene and 45 °C, the system gave a selectivity to C_8 of 68.3 %, of which 98.9 % is 1-octene and a productivity of 272,400 g (g Cr h)$^{-1}$. Ligands with bulky alkyl groups on the nitrogen (reaction 1.35, and 1.36 in Table 1.12) gave about 50 % 1-octene selectivity at 65 °C and 30 bar of ethene. Ligand **18** (reaction 1.36 in Table 1.12) gave promising results with respect to selectivity to α-alkenes, with selectivities to 1-hexene and 1-octene of 86.1 % and 99.3 % respectively within the C_6 and C_8 fractions. This suggests that α-branching of substituents on the nitrogen has a key effect on the selectivity towards α-alkenes.

Due to the success of ligand **19** with an isopropyl group on the nitrogen, this research was extended to PNP ligands with various bulky substituents on the nitrogen, a selection of which are shown in Figure 1.9 and the results from these ligands are shown in Table 1.13.[50]



20 - R^1=R^2=H
21 - R^1=Me, R^2=H
22 - R^1=*i*Pr, R^2=H
23 - R^1=H, R^2=*t*Bu
24 - R^1=H, R^2=OMe



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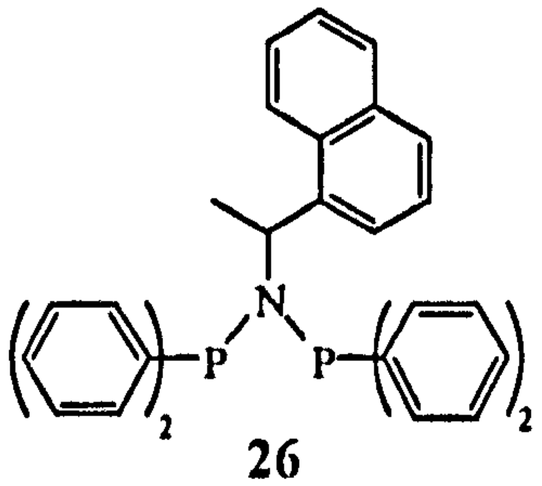

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Figure 1.9 – PNP With Phenyl Derivatives on Nitrogen Backbone

Table 1.13 – Tetramerisation PNP Ligands in Figure 1.9

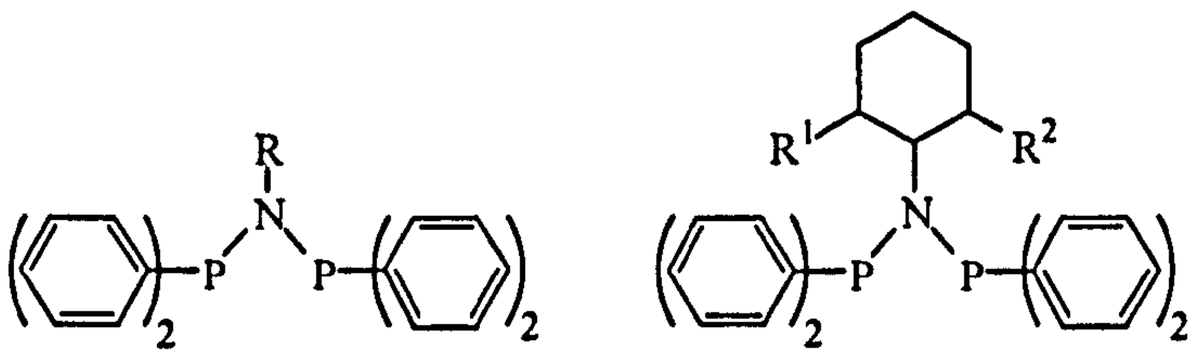
Reaction	Ligand	Time / mins	Productivity / g (g Cr h)$^{-1}$	Selectivity (wt %)					
				C_6	1-C_6[a]	C_8	1-C_8[b]	C_{10+}	PE
1.38	**20**	12	765,900	16.6	54.2	61.8	97.1	17.2	3.3
1.30	**21**	18	526,700	27.1	56.6	56.8	97.0	9.9	4.8
1.40	**22**	45	159,600	33.4	86.2	52.9	99.2	6.0	7.8
1.41	**23**	9	1,146,200	17.7	53.5	62.3	96.6	16.4	1.9
1.42	**24**	26	385,900	22.1	40.2	58,2	96.7	13.8	4.6
1.43	**25**	9	1,065,300	18.8	46.5	63.5	97.2	14.4	1.3
1.44	**26**	9	1,012,900	27.1	82.1	62.8	99.2	8.9	0.8

0.01 mmol [$Cr(acac)_3$], 0.01 mmol PNP Ligand, 480 eq MMAO, 60 °C, 50 bar ethene; [a] selectivity to 1-C_6 within C_6 fraction; [b] selectivity to 1-C_8 within C_8 fraction

Table 1.13 shows data from trimerisation or tetramerisation of ethene using PNP ligands with aromatic groups on the nitrogen backbone in Figure 1.9. Ligand **20** (reaction 1.38 in Table 1.13) with a phenyl group on the nitrogen, produced a productivity of 765,900 g (g Cr h)$^{-1}$ and a selectivity to 1-C_8 of 97.1 % within the C_8 fraction and an overall selectivity to 1-octene of 60.0 %. Increasing the size of R^1 from a hydrogen to a methyl group (ligand **21**, reaction 1.39 in Table 1.13) and then an isopropyl group

(ligand **22**, reaction 1.40 in Table 1.13) decreases the productivity and selectivity to C_8, increasing the percentage of C_6 produced. The group also investigated electronic effects by testing ligands **23** and **24**. Ligand **23** (reaction 1.41 in Table 1.13) has an electron rich tertiary butyl (*t*Bu) group in the *para* R^2 position, this lead to a higher productivity of 1,146,200 g (g Cr h)$^{-1}$ compared to ligand **20** but had little effect on selectivity. Having an OMe group in the R^2 position in ligand **24** (reaction 1.42 in Table 1.13), the productivity was greatly reduced.[50]

Ligands **25** and **26** (reactions 1.43 and 1.44 in Table 1.13) show ligands with a carbon spacer between the nitrogen and the phenyl group. Using ligand **25** did not improve the selectivity over ligand **20**, although the productivity was increased to 1,065,300 g (g Cr h)$^{-1}$. Ligand **26** gave the best results with respect to productivity and selectivity, for this group, with a productivity of 1,012,900 g (g Cr h)$^{-1}$, and a selectivity to C_6 of 27.1 %, (1-C_6 of 82.1 %) and to C_8 of 62.8 %, of which 99.2 % was 1-C_8. It was concluded that the steric bulk of the phenyl group on the nitrogen had a significant effect on the selectivity to α-alkenes (1-C_6 and 1-C_8). The productivities obtained in this study are comparable to the ethene trimerisation system $[CrCl_3(thf)_3]$/ligand **1**, developed by Wass and co-workers, although a high pressure is needed for trimerisation or tetramerisation to occur.[4]



27 - R = cyclopentyl
28 - R = cyclododecyl

29 - R^1=H, R^2=Me
30 - R^1=R^2=Me

Figure 1.10 – PNP Ligands with Bulky Groups on Nitrogen

Table 1.14 – Tetramerisation PNP Ligands With Ligands in Figure 1.10

Reaction	Ligand	Time / mins	Productivity / g (g Cr h)$^{-1}$	Selectivity (wt %)					
				C_6	1-C_6[c]	C_8	1-C_8[d]	C_{10+}	PE
1.45[a]	**27**	28	544,629	18.6	63.9	63.7	98.1	15.7	2.0
1.46[a]	**28**	25	757,720	22.6	84.6	66.4	99.4	9.6	0.9
1.47[b]	**29**	15	2,279,200	26.6	85.4	63.7	99.5	8.9	0.8
1.48[b]	**30**	13	2,134,983	43.0	95.4	48.7	99.7	8.0	0.3

[a] 0.025 mmol [$Cr(acac)_3$], 0.025 mmol PNP Ligand, 540 eq MMAO, 60 °C, 45 bar ethene, 100 mL cyclohexane; [b] 0.05 mmol [$Cr(acac)_3$], 0.075 mmol PNP Ligand, 2700 eq MMAO, 60 °C, 45 bar ethene, 100 mL methylcyclohexane; [c] selectivity to 1-C_6 within C_6 fraction; [d] Selectivity to 1-C_8 within C_8 fraction

Table 1.14 shows the results obtained from having bulky non-aromatic groups on the nitrogen in the PNP backbone in Figure 1.10.[51] Ligands **27** (reaction 1.45 in Table 1.14) with a cyclopentyl group on the nitrogen produced high selectivities to C_8 fraction, with selectivities to 1-C_8 of 98.1 % respectively, although the selectivity to 1-C_6 within the C_6 fraction was low. The selectivity to 1-C_6 within the C_6 fraction is increased for ligand **28** (reaction 1.46 in Table 1.14), with a productivity of 757,720 g (g Cr h)$^{-1}$. Ligand **29** and **30** (reaction 1.47 and 1.48 in Table 1.14) showed the best results with productivities of over 2 million g (g Cr h)$^{-1}$ at 60 °C and 45 bar of ethene. The selectivities to 1-C_6 and 1-C_8 were also high, although the selectivity towards the C_8 fraction for ligand **29** was reduced compared to the other examples.

McGuinness and group found that treatment of chromium/ligand systems or preformed complexes with trialkylaluminium and a stoichiometric amount of either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ provided active catalysts.[52] A range of PNP ligands were tested and it was found that activation with AlR_3 and the borate produced a distribution of oligomers similar to that of MAO, although productivity was reduced and the amount of polymer produced increased. Using $AlEt_3$, with $B(C_6F_5)_3$, was more effective than $AlMe_3$ and the productivity was higher at 45 °C than 60 °C. A selection of results is shown in Table 1.15.[52]

Table 1.15 – Trimerisation/Tetramerisation with Borate Cocatalysts

Reaction	Ligand	AlR_3	Cocatalyst	Productivity / g (g Cr h)$^{-1}$	Selectivity (wt %)				
					C_6	1-C_6[a]	C_8	1-C_8[b]	PE
1.49	18	$AlEt_3$ (30 eq)	$B(C_6F_5)_3$	12,560	16.0	69.0	62.1	98.3	13.0
1.50	18	$AlEt_3$ (100 eq)	$B(C_6F_5)_3$	1,174	21.4	73.3	47.6	96.9	25.2
1.51	18	$AlEt_3$ (50 eq)	$[Ph_3C][B(C_6F_5)_4]$	5,190	17.3	71.4	62.2	98.9	15.8

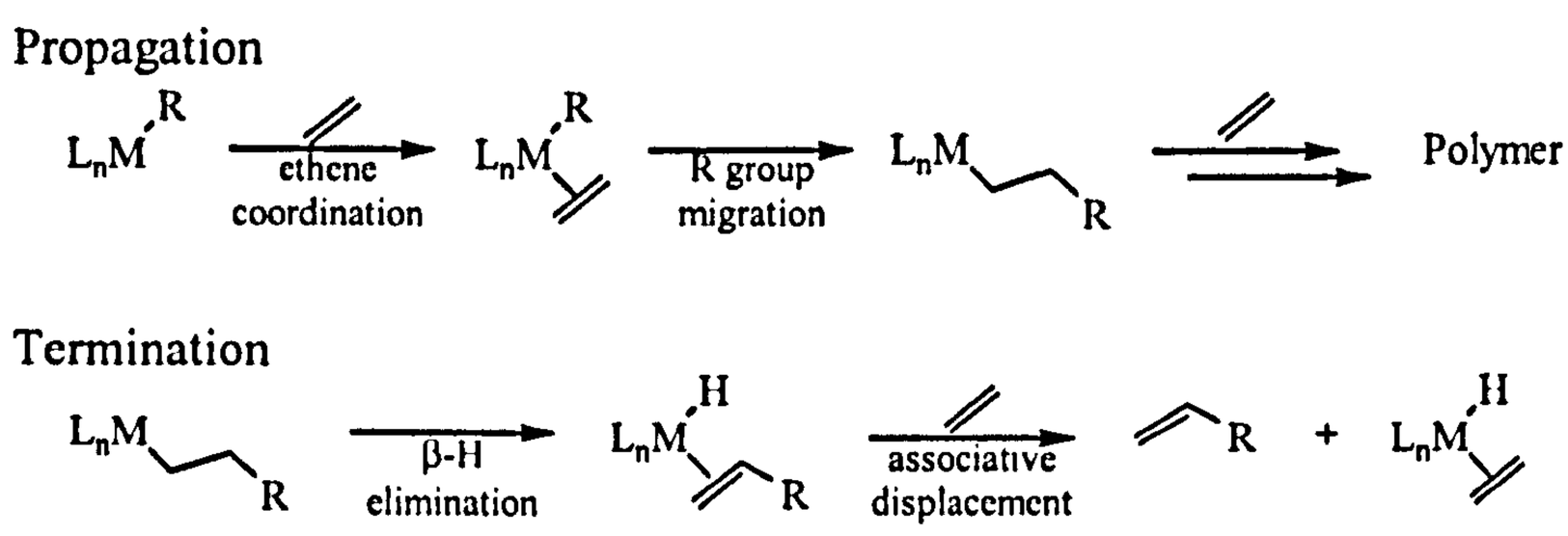
0.01 mmol $[CrCl_3(thf)_3]$, 0.012 mmol PNP Ligand, 0.01 mmol borate cocatalyst, 100 mL toluene, 50 bar ethene, 45 °C, 30 min run time; [a] selectivity to 1-C_6 within C_6 fraction; [b] Selectivity to 1-C_8 within C_8 fraction.

The selectivity to 1-hexene within the C_6 fraction and 1-octene within the C_8 fraction is not affected by the borate cocatalyst and is still controlled by the ligand. This suggests that the environment of the Cr centre remains the same as when activated with MAO. Using $[Ph_3C][B(C_6F_5)_4]$ (reaction 1.51 in Table 1.15) produces an active catalyst although the productivity was greatly reduced, this cocatalyst was more stable to excess $AlEt_3$ than $B(C_6F_5)_3$. Rapid deactivation of the $[Ph_3C][B(C_6F_5)_4]$/$AlEt_3$ system was observed and the rate of ethene trimerisation/tetramerisation decreased. $Al(i\text{Bu})_3$ was also tested and an increase in the selectivity to polymer (50.6 %) was observed. Increasing the amount of $[Ph_3C][B(C_6F_5)_4]$ to 5 equivalents caused an increase in productivity, although a Schultz Flory distribution of α-alkenes was produced. Further investigations showed that when a higher amount of borate cocatalyst was used, the PNP ligand has little influence on the selectivity and productivity of the system. It is suggested that the borate reacts with the PNP ligand and causes rearrangement of the ligand structure. There is a fine balance between a system that can tetramerise ethene and trimerise ethene and also the selectivities towards α-alkenes obtained within the C_6 and C_8 fractions.

1.4. Mechanism and Activation

1.4.1. Ethene Trimerisation

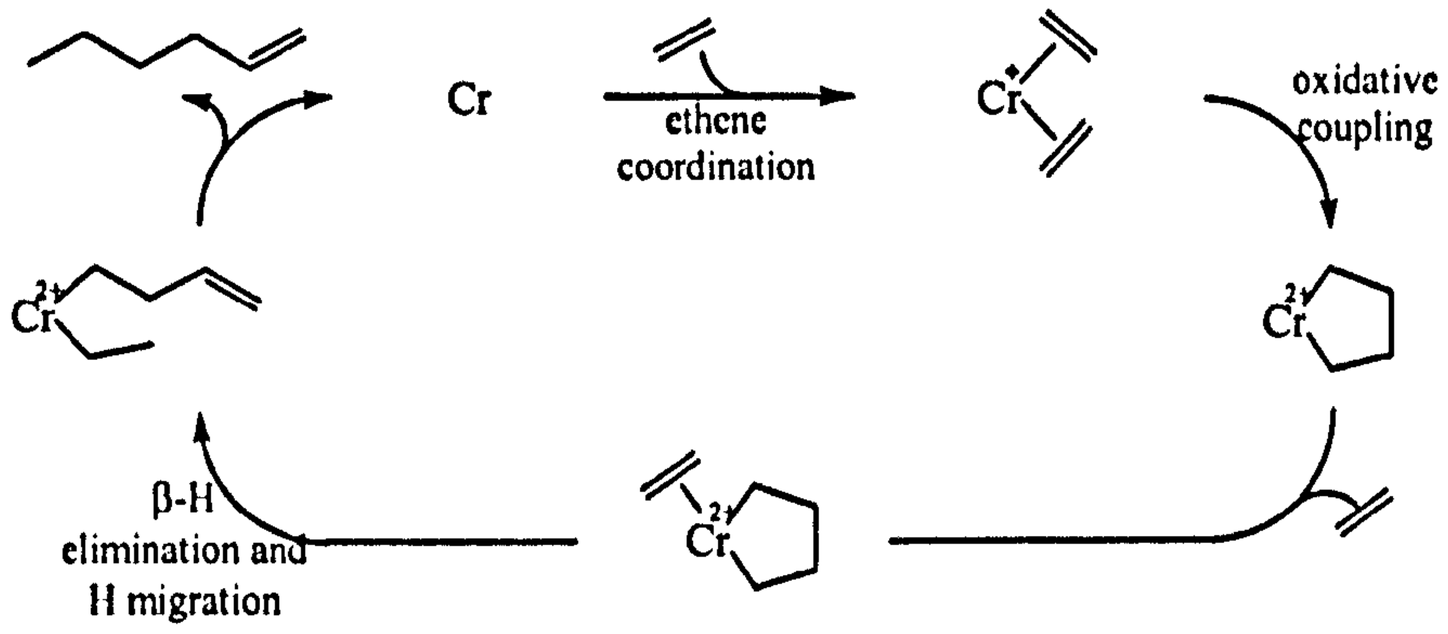
In 1964 Cossee and Arlman proposed a mechanism for the polymerisation of α-alkenes based on early transition metals.[48, 53, 54] The proposed mechanism is outlined in Scheme 1.11.



Scheme 1.11 – Cossee Mechanism for Polymerisation of Ethene

In this mechanism ethene coordinates to the metal centre, where R is the growing polymer chain. Next migratory insertion takes place increasing the chain length, and leading to propagation. Termination or chain transfer occurs *via* β-hydride elimination, followed by displacement of the α-alkene with ethene. The size of the carbon chain is controlled by the rate of termination relative to the rate of propagation, therefore smaller α-olefin oligomers are produced when the rate of termination is equal to or greater than that of propagation. This mechanism always produces a Schultz-Flory distribution of oligomers and so cannot explain a catalyst system which is highly selective to trimer products. The case of apparently selective dimerisation is observed in some systems; however this is the result of the same mechanism when the rate of termination is greater then the rate of propagation.[48, 53, 54]

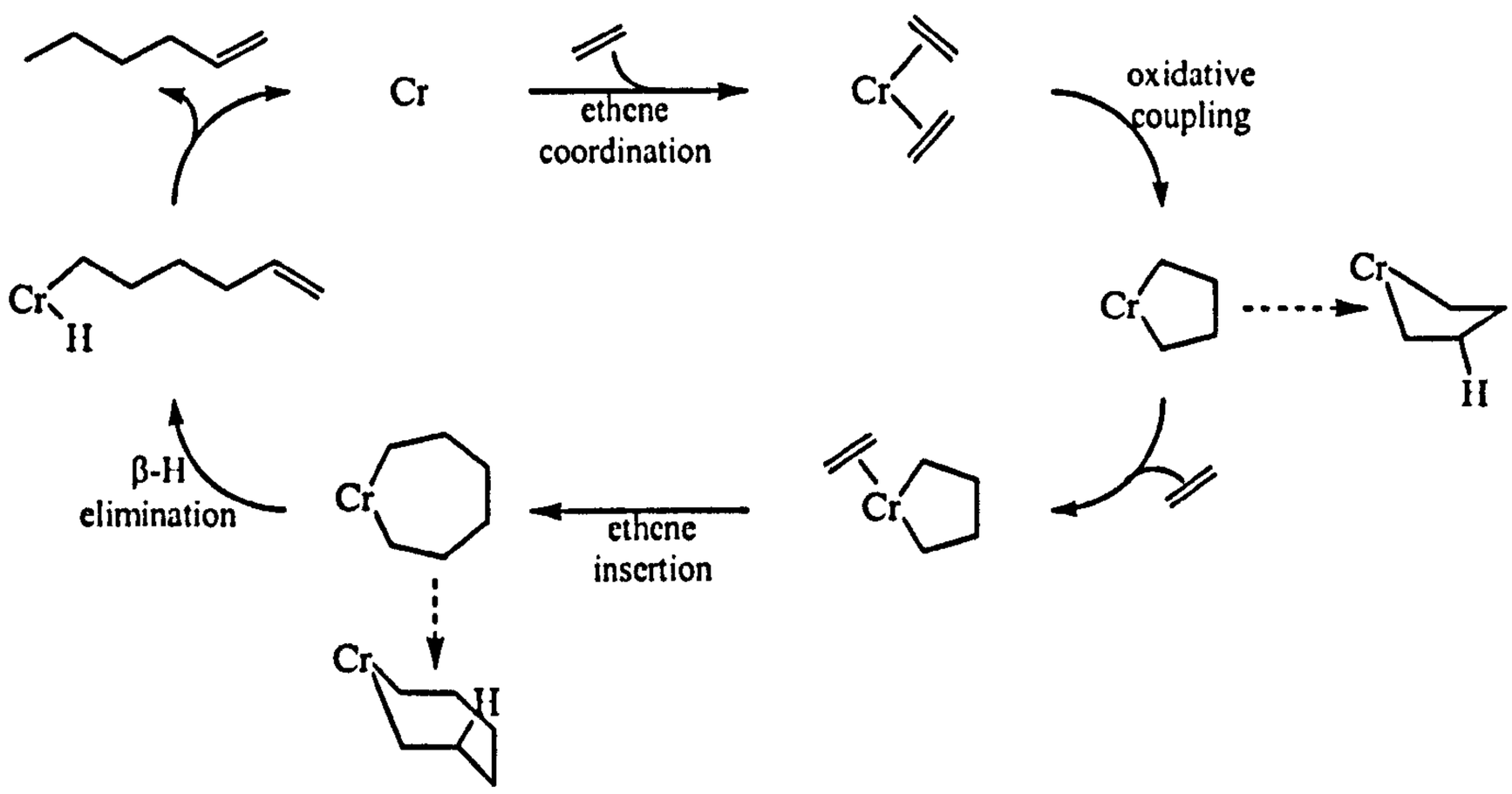
In the early 1970s, McDermott found evidence of Pt(II) metallacycles, showing that metallacycles could exist as reaction intermediates.[55] Building on this observation, an ethene trimerisation mechanism involving metallacycles was proposed by Manyik in 1977, as shown in Scheme 1.12.[6]



Scheme 1.12 – Mechanism Proposed by Manyik

Manyik proposed that two ethene molecules coordinate to the chromium centre and oxidative coupling takes place to form a five membered metallacycle. This is followed by a β–hydrogen transfer from the metallacycle to a third ethene molecule, giving the chromium butenyl ethyl intermediate. Lastly reductive elimination causes the release of 1-hexene.[2, 6]

Briggs suggested that instead of β-hydrogen transfer occurring, a chromium metallacycloheptane is formed as shown in Scheme 1.13.[56]



Scheme 1.13 – Postulated Mechanism by Briggs for Ethene Trimerisation

In this mechanism, after formation of the chromium metallacyclopentane, a third ethene molecule coordinates to the metal centre and inserts into the metal-carbon bond, forming the seven membered metallacycle. Next β–hydride elimination occurs to form the chromium alkyl hydride species. Finally 1-hexene is eliminated *via* reductive elimination and the catalyst is regenerated. This mechanism is now generally accepted.

For selective 1-hexene formation, the rate of insertion of ethene into the chromium metallacyclopentane must be faster then the breakdown of the metallacycle to 1-butene. The geometric constraints on the metallacyclopentane mean that ethene insertion is more favourable than β-hydride elimination to form 1-butene, thus forming a barrier against 1-butene formation. Whereas metallacycloheptane is more flexible and so β-hydride elimination readily occurs to form 1-hexene.[2]

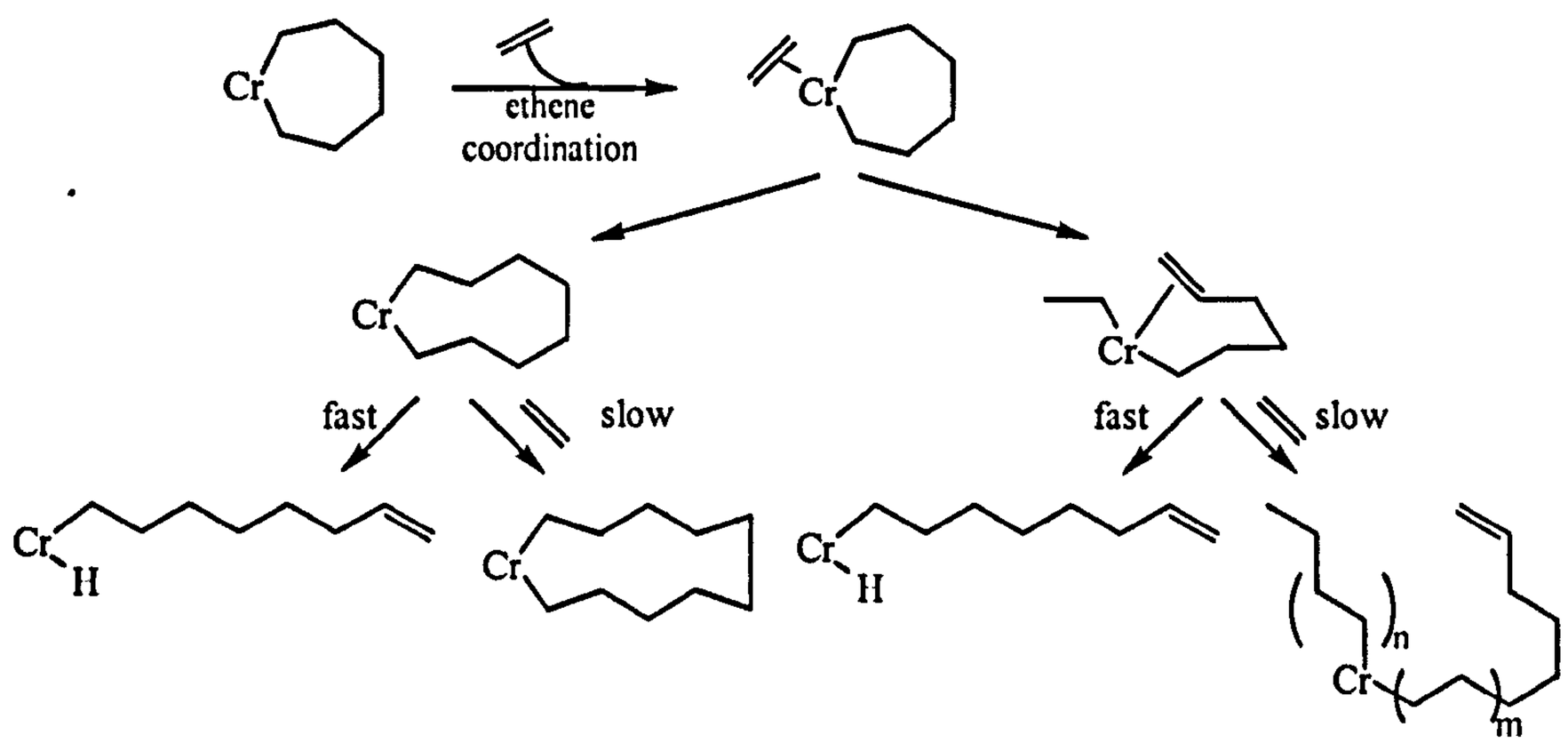
Good evidence for the metallacycle mechanism has been published. Bercaw and co-workers investigated the mechanism by carrying out trimerisation on a 1:1 mixture of C_2D_4 and C_2H_4.[5] The group predicted that the metallacycle route, in Scheme 1.13, would produce no H/D scrambling, giving a limited range of 1-hexene isomers, C_6H_{12}, $C_6D_8H_4$, $C_6D_4H_8$, C_6H_{12}, whereas the Cossee mechanism would cause H/D scrambling and the isomers of 1-hexene produced would have an odd number of deuterium atoms. The catalytic system used was $[CrPh_3(\mathbf{1})]$, **7**, Figure 1.4 and $[H(Et_2O)][B(C_6H_3(CF_3)_2)_4]$ and as postulated it yielded isomers of 1-hexene with even numbers of deuterium atoms. The existence of five and seven membered metallacycles of chromium was reported by Jolly with studies on η^5-cyclopentadienyl-stabilised chromacyclopentane and chromacycloheptane complexes.[57]

There has been much debate on the change in oxidation states in the catalytic cycle. First it is thought that the precatalyst is reduced by activation. Next the formation of the metallacycle changes the oxidation state from M^n to M^{n+2}, and then returns back to M^n on liberation of 1-hexene. Manyik[6] and Kohn[58] both proposed a Cr(I)/(III) system, Cr(II)/(IV)[59-61] and Cr(III)/(V)[62] systems have also been proposed. The oxidation state of the metal centre is explained further in Section 1.5.3.3.

There is evidence of 1-hexene being incorporated back into the trimerisation mechanism from the production of C_{10} and C_{14} alkenes. Wass and co-workers demonstrated that adding 1-butene to the reaction, shown in Scheme 1.8 increased the amount of C_8 materials, which is due to the incorporation of 1-butene into the product. As the reaction proceeds the relative weight percentage of C_{10} and C_{14} materials produced increases due to the increasing concentration of hexene.[4]

1.4.2. Ethene Tetramerisation

It was initially thought that tetramerisation was not possible as the formation of a nine membered metallocycle intermediate would have to take place *via* insertion of ethene into the chromacycloheptane. Houk suggested that the formation of metallacyclononane is unlikely, due to a nine membered ring being the ring size with the highest strain.[49] McGuinness and co-workers suggested that as the selectivities towards 1-hexene and 1-octene can be controlled by slight PNP ligand modifications, it can be hypothesised that the common metallacycloheptane is involved in trimerisation and tetramerisation.[63] A mechanism is suggested where 1-octene can be formed by either of two routes, this is shown in Scheme 1.14.

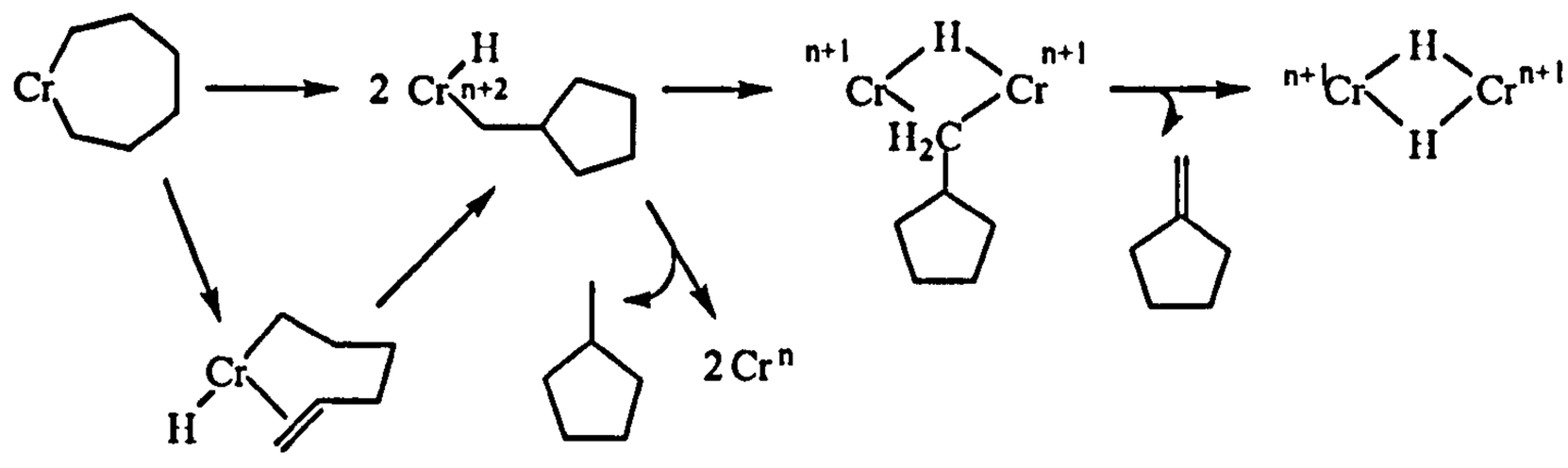


Scheme 1.14 – Proposed Mechanism for Ethene Tetramerisation

Tetramerisation reactions also form higher 1-alkenes, which may be derived from the extension of metallacyclononane, *via* further insertion of ethene. It was found that the

distribution of higher 1-alkenes was not consistent with a linear chain growth mechanism and was consistent with the metallacycle mechanism. Also the group found that metallacyclononane (Cr-C_8) is the least stable metallacycloalkane, with Cr-C_{12} and Cr-C_{14} being the most stable, this contribute to the higher selectivity to 1-octene.[63, 64]

Further work showed that methylene cyclopropane and methylcyclopropane were the major side products. These two side products are derived from the formation of a chromium cyclopentylmethyl hydride species, as shown in Scheme 1.15.[63]



Scheme 1.15 – Formation of Methylcyclopropane and Methylenecyclopropane

It was hypothesised that the formation of methylcyclopropane and methylenecyclopropane occurs *via* a binuclear mechanism as shown in Scheme 1.15, the two products are always formed in a ratio of 1:1.[63]

1.4.3. Catalyst Activation

To form a catalyst, the precatalyst undergoes activation by the addition of a cocatalyst, which also acts as a weakly coordinating anion. The cocatalyst used can have a significant effect on activity, stability and selectivity. Alkylaluminium compounds are commonly used, including trimethylaluminium (TMA), TEA and aluminoxanes, such as methylaluminoxane (MAO). Other trimerisation/tetramerisation cocatalysts are perfluoroaryl borates, trityl borates and ammonium borates. Although other metal alkyls, for example Li, Sn and Zn can also be used.[2, 65] The cocatalyst assists alkyl abstraction from the catalyst precursor giving an cationic metal fragment [L_nM] and an anionic cocatalyst fragment [RX], giving the active catalyst [L_nM][RX].[66]

1.4.3.1. Structure of MAO

One of the most common activators used in ethene trimerisation/tetramerisation is methylaluminoxane (MAO). Alkylaluminoxanes have been known to activate the polymerisation of monomers such as oxiranes since the 1960s and consist of –Al(R)-O- units, where R is an alkyl chain.[67] MAO has the formula $[-Al(Me)-O-]_n$ ($n \approx 5$-20) and is prepared by controlled hydrolysis of $AlMe_3$. The exact structure of MAO is still unknown but it is thought to consist of one dimensional linear chains or cyclic rings with one, two or three dimensions. A selection of proposed structures of MAO are shown in Figure 1.11.[65, 66]

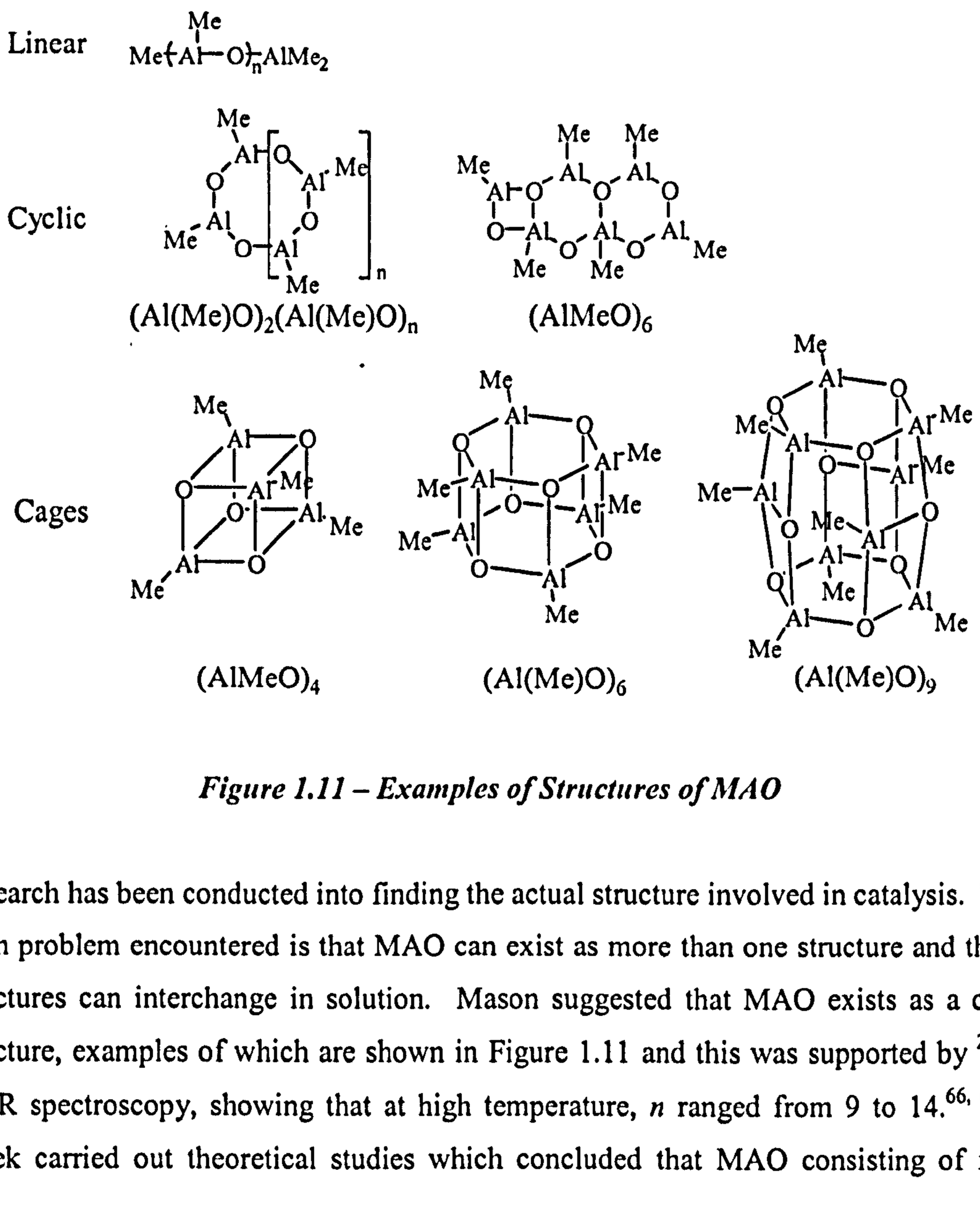
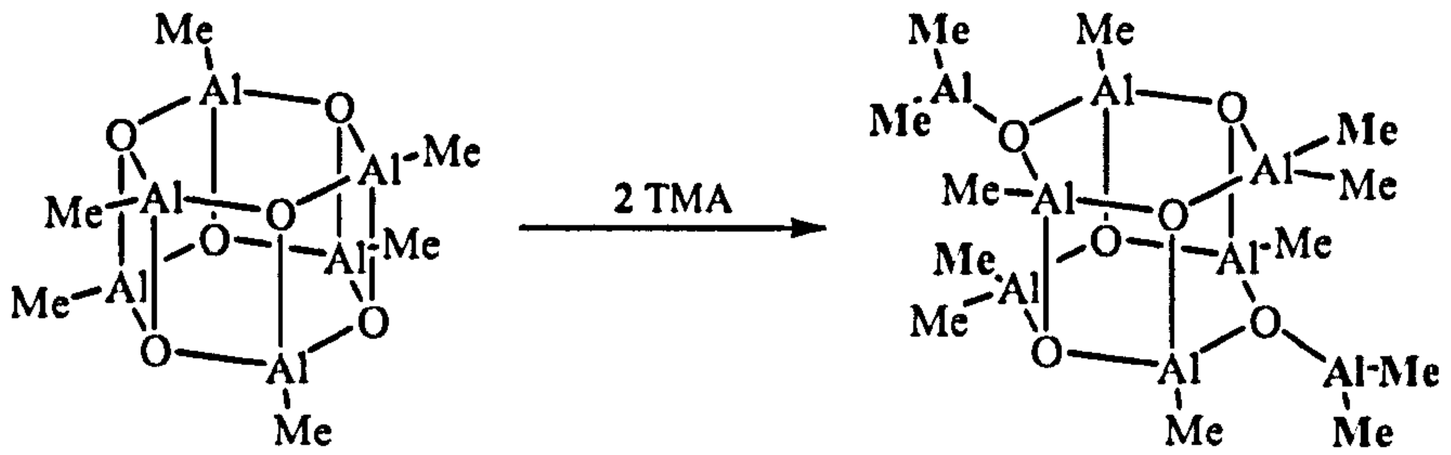


Figure 1.11 – Examples of Structures of MAO

Research has been conducted into finding the actual structure involved in catalysis. The main problem encountered is that MAO can exist as more than one structure and these structures can interchange in solution. Mason suggested that MAO exists as a cage structure, examples of which are shown in Figure 1.11 and this was supported by ^{27}Al NMR spectroscopy, showing that at high temperature, *n* ranged from 9 to 14.[66, 68-70] Zurek carried out theoretical studies which concluded that MAO consisting of four

coordinate aluminium and three coordinate oxygen, in three-dimensional cages is more stable than linear chains or rings.[66, 71, 72] Zurek also found that cages consisting of square and hexagonal faces are the most stable and cages where two square faces meet are disfavoured, meaning that the most abundant cage is $(Al(Me)O)_{12}$.[71, 72]

For MAO systems to be catalytically active, residual TMA is also needed, implying that the ratio of Al:O:Me is not 1:1:1 and that TMA may be incorporated into the MAO cage structure.[73] Research by Imhoff showed that the composition of MAO is $(AlO_{0.75\text{-}0.8}Me_{1.4\text{-}1.5})$.[74] An example of the incorporation of TMA into the MAO cage structure is shown in Figure 1.16.[66]



$(Al(Me)O)_6$ $(Al(Me)O)_6(TMA)_2$

Scheme 1.16 – Incorporation of TMA into MAO Cage Structure

Zakharov reported a general equation for the amount of TMA incorporated into the MAO structure, Equation 1.1.[75]

$$(Al(Me)O)_n + \tfrac{1}{3}\,n\,AlMe_3 \rightarrow (AlMe_{1.5}O_{0.75})_{n+\frac{1}{3}n} \qquad \text{Equation 1.1}$$

Van Rensburg and co-workers conducted research on the interaction between MAO and metallacycloheptane in the trimerisation mechanism using $[CrCl_3(thf)_3]$/19/MAO as the catalytic system.[66] It was found that MAO interacts with the chromacycloalkanes in the mechanism and that the size of the MAO cage influences this interaction. The cages with TMA incorporated contain three coordinate Al centres and show more Lewis acidity, which in turn interact with the chromacycloheptane *via* bridging Me groups. Figure 1.12 shows a diagram derived from a DFT study into the interaction between

MAO and metallacycle, the two diagrams are examples of structures with optimized geometry and show the zero point energy (ΔE_{ZPE}).

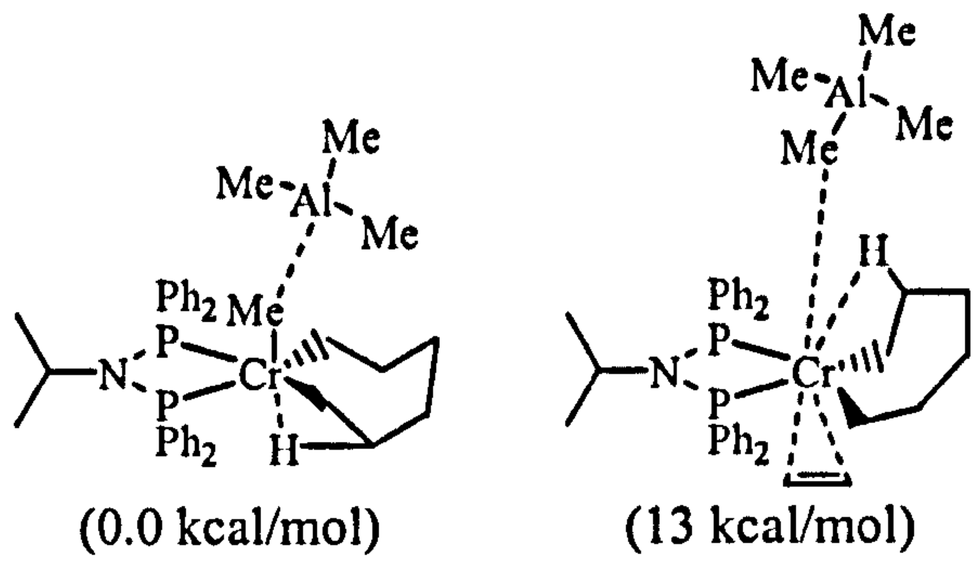
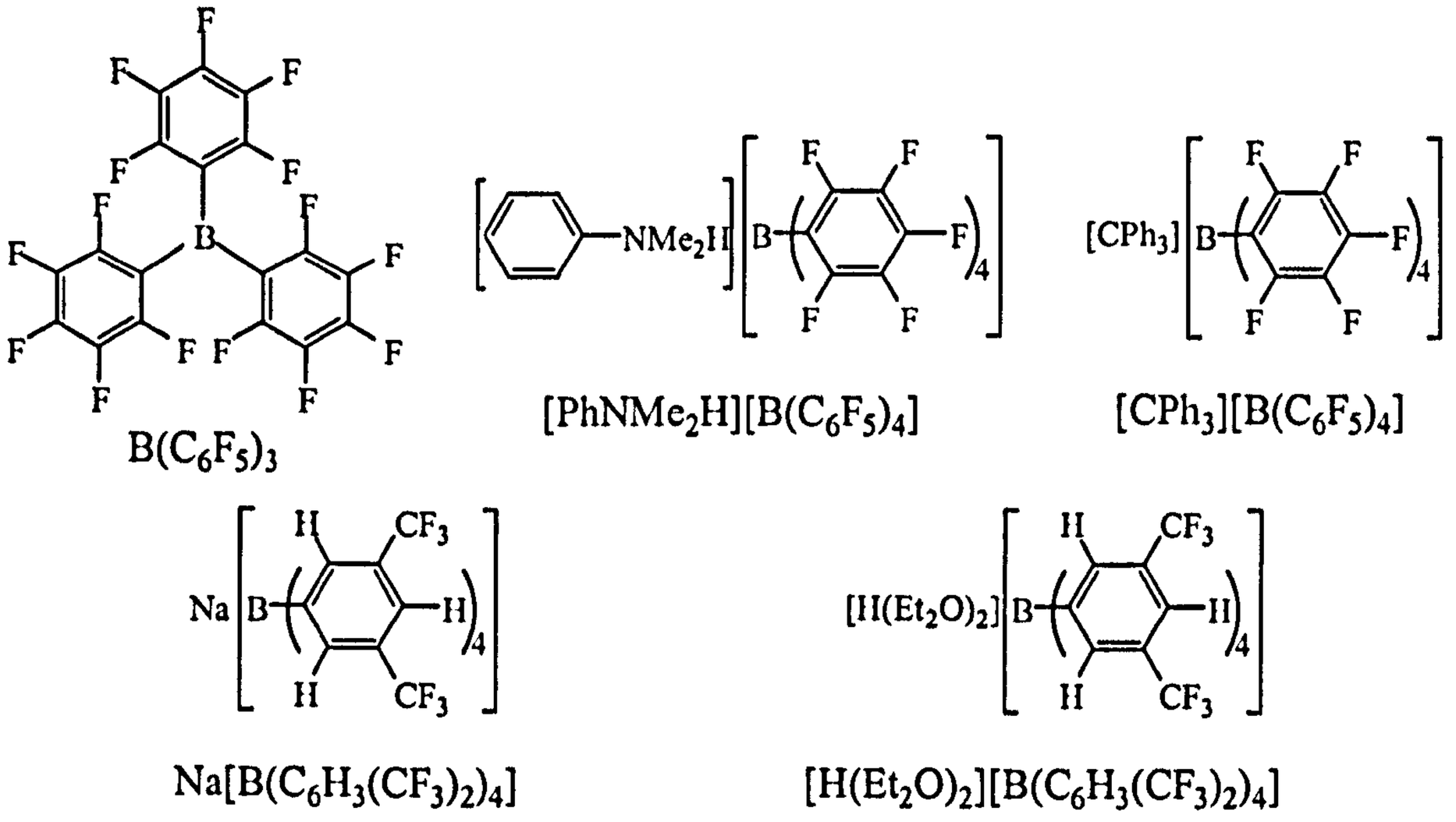


Figure 1.12 – DFT Studies – Optimised Geometries for MAO Interaction with Chromacycloheptane

1.4.3.2. Borate Activators

In the 1990s Marks and Ewen discovered that the strong Lewis acid tris(pentafluorophenyl)borate, $B(C_6F_5)_3$, in conjunction with an early transition metal allyl complex, promoted ethene polymerisation.[76, 77] Therefore this class of activators was tested for the trimerisation of ethene, a selection are shown in Figure 1.13.[65]



$B(C_6F_5)_3$

$[PhNMe_2H][B(C_6F_5)_4]$

$[CPh_3][B(C_6F_5)_4]$

$Na[B(C_6H_3(CF_3)_2)_4]$

$[H(Et_2O)_2][B(C_6H_3(CF_3)_2)_4]$

Figure 1.13 – (Perfluoroaryl)borate Co-catalysts

(Perfluoroaryl)borate activators are generally used if a transition metal alkyl or aryl catalyst precursor is used as the catalyst precursor, for example $[H(Et_2O)_2][B(C_6H_3(CF_3)_4]$ is used to activate $[CrPh_3(1)]$, **7**.[5] These Lewis acid compounds contain a weakly coordinating anion, which stabilises the formation of the active catalyst but enable catalysis to occur by leaving a vacant site on the metal. An advantage of using borate activators is a well defined system is produced, where molecular structures can be obtained and therefore investigations into the catalyst mechanism can be carried out. Studies show that the choice of counterion has a pronounced effect on catalyst stability, activity and selectivity, due to the metal-anion interaction.[5]

1.4.3.3. Formation of Active Catalyst

This section explains how aluminoxanes, mainly MAO, alkyl aluminium compounds and borates are used to activate precatalysts to form the active catalyst.

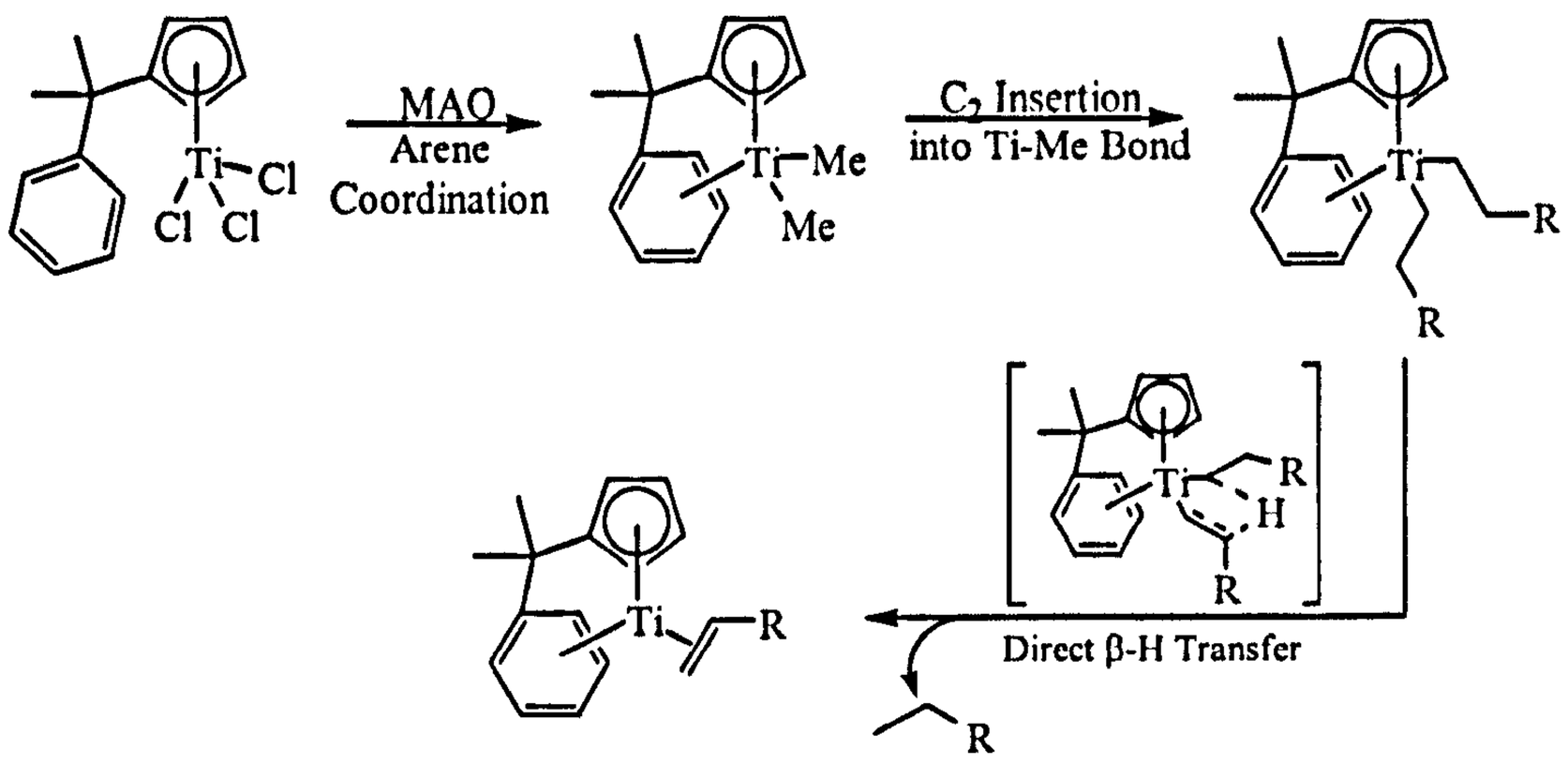
In the $[CrCl_3(thf)_3]$/1/MAO system developed by Wass and co-workers, catalyst activation is achieved by reduction of Cr(III) to Cr(I).[1, 4] The speculated mechanism by which the reduction may occur is shown in Scheme 1.17.

$$(1)CrCl_3 \xrightarrow{MAO} Cr^{III}Me_3 \xrightarrow{\text{- Me-MAO}} Cr^{III}Me_2^{+} \xrightarrow{-C_2H_6} Cr^{I+}$$

Scheme 1.17 – Activation of Catalyst with MAO

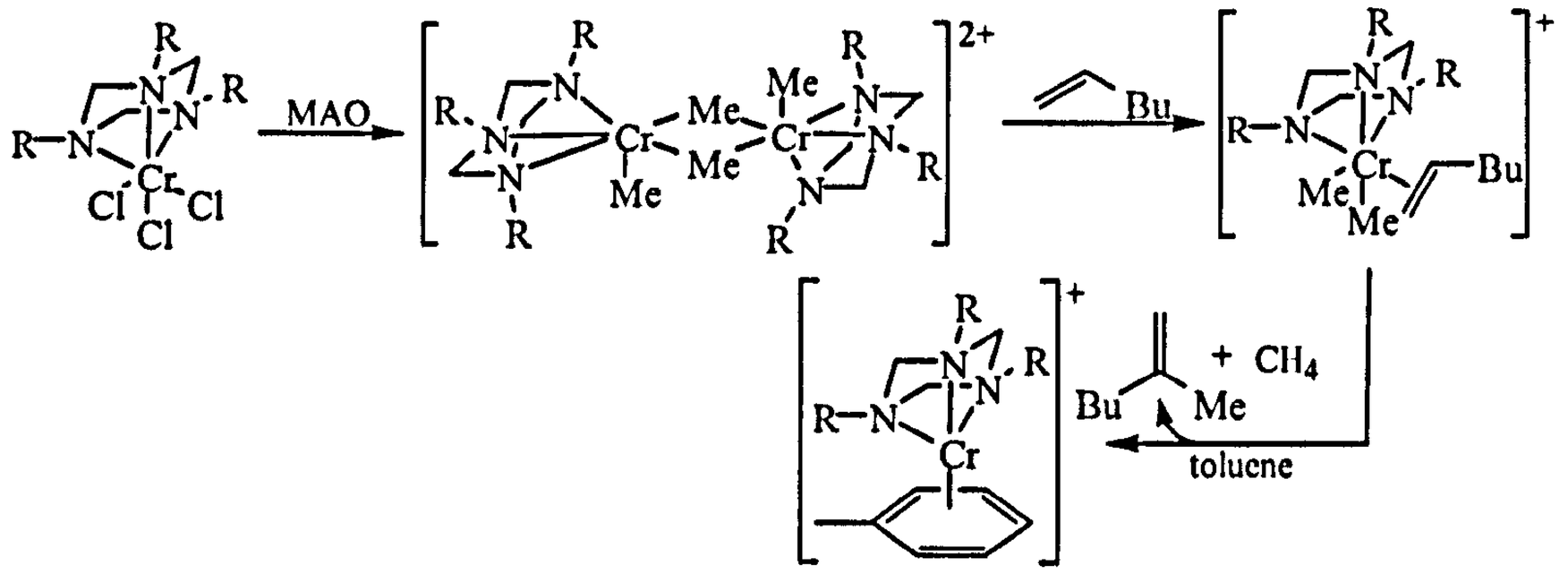
Firstly MAO methylates the chromium centre, giving $[Cr(III)Me_3]$, followed by extraction of one methyl group to give $[Cr(III)Me_2]^+$. Reductive elimination occurs to give the active Cr(I) centre, leaving a vacant site on the metal for ethene coordination. It has been suggested that the formation of Cr-Me species is not due to MAO but due to residual TMA and that the reduction of Cr(III) to Cr(I) may also be due to residual TMA.[66] A similar method of activation was initially proposed by Hessen.[45, 46] This group suggested that the activation of $[Ti^{IV}Cl_3(C_5H_4C(CH_3)_2C_6H_3)]$ to an active Ti(II) species with MAO occurs *via* a $[Ti^{IV}(C_5H_4C(CH_3)_2C_6H_3)Me_2]^+$ species. Blok modified this mechanism showing that the active Ti(II) species could be generated by an agostic

assisted β-hydrogen transfer step from Ti(IV) dialkyl species (Scheme 1.18), this route was calculated to be the lowest energy pathway.[51]



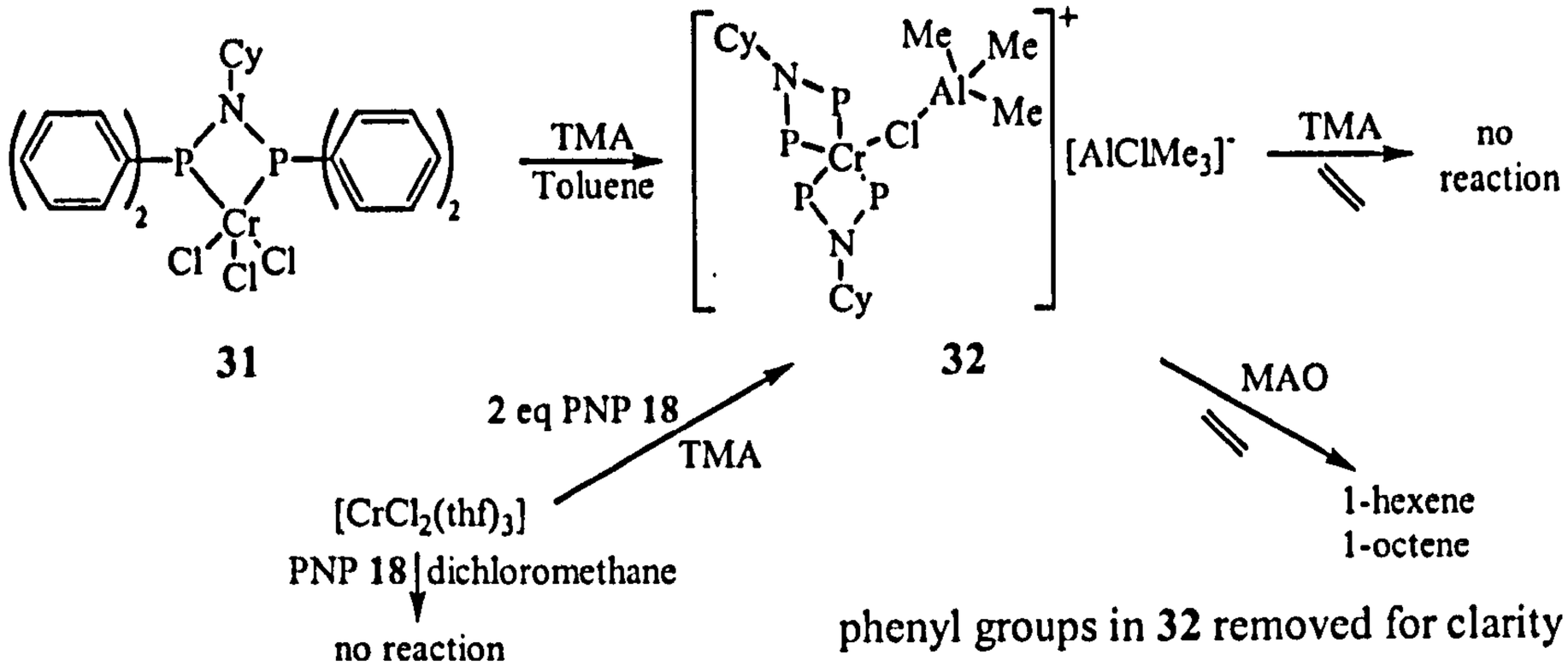
Scheme 1.18 – Activation of [$Ti^{IV}Cl_3(C_5H_4C(CH_3)_2C_6H_3)$]

Köhn and co-workers[58, 78] and Bercaw and co-workers[5] have produced work supporting this mechanism. Köhn proposed that the activation of chromium triazacyclohexane complexes proceeds *via* a methyl bridged dinuclear Cr intermediate, see Scheme 1.19. The insertion of 1-hexene cleaves all methyl bridges, followed by β-hydrogen transfer and reductive elimination forms the active catalyst, with the release of 2-methyl-1-hexene and methane.



Scheme 1.19 – Activation of Chromium Triazacyclohexane Complexes With MAO

Gambarotta and co-workers synthesised a cationic chromium(II) PNP species and the complex was tested for trimerisation with TMA and MAO, as shown in Scheme 1.20.[79]



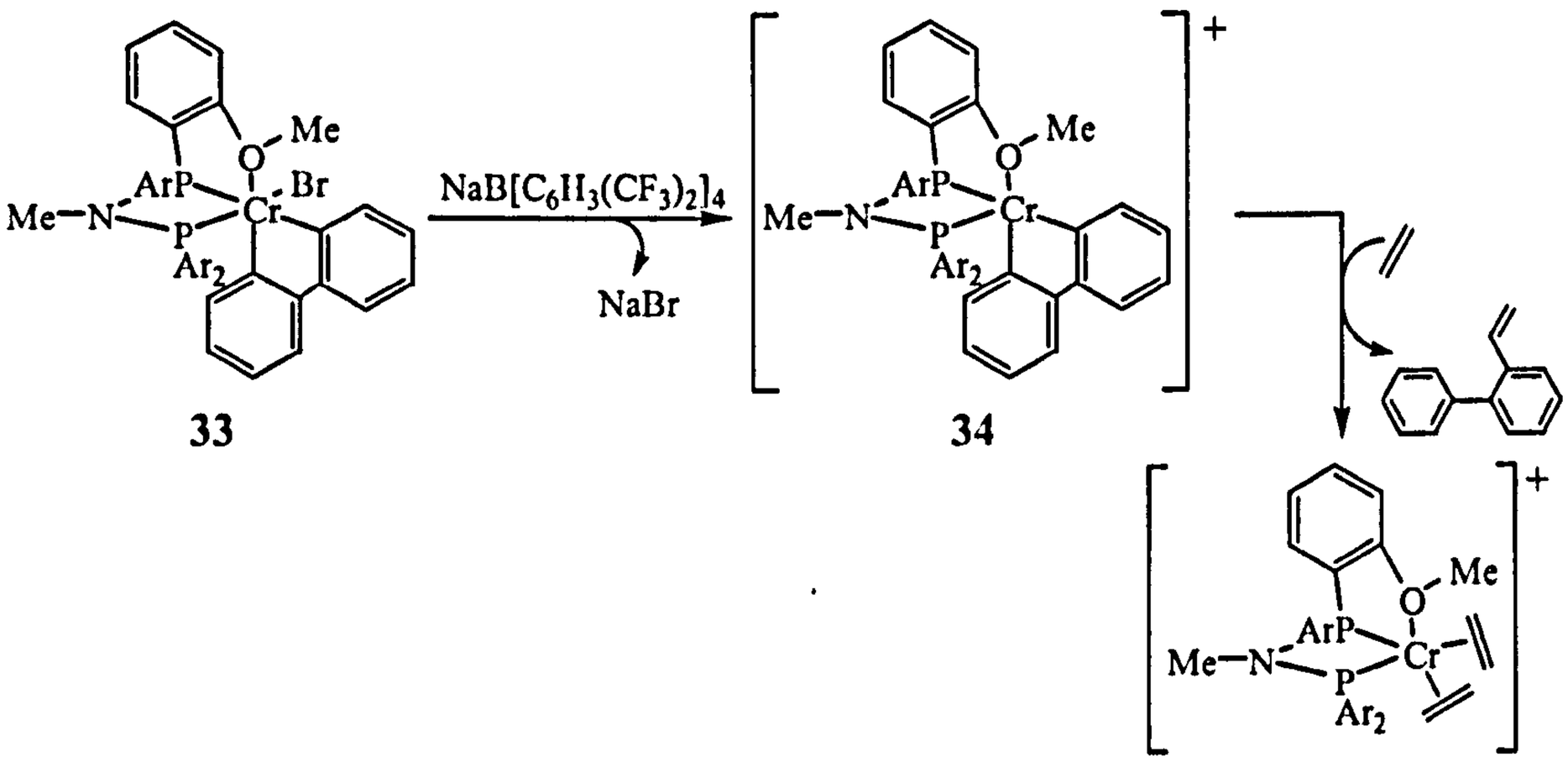
Scheme 1.20 – Activation of $[Cr^{II}(AlMe_3)Cl(18)_2][AlClMe_3]$ with MAO or TMA

Complex **32** was synthesised from **31** and isolated and tested for ethene tetramerisation, upon activation with MAO, the system gave an activity of 8,400 g (g Cr h)$^{-1}$, which is comparable to the $[CrCl_3(thf)_3]$/**18**/MAO system (reaction 1.36 in Table 1.12).[69] It was concluded that, although further reduction of the chromium centre cannot be ruled out, the reduction of the metal centre is a step in the activation of the catalyst precursor. There are two ligands present in complex **32**, suggesting that 50 % of the catalyst precursor is being converted to another unknown species. Ligand **18** only reacts with $[CrCl_2(thf)_3]$ in the presence of TMA, implying that the stability of complex **32** depends on the presence of two PNP ligands and an alkylating agent. Trimerisation only occurs when MAO is used and not just TMA, supporting the theory that it is the TMA residue in MAO that reduced the precatalyst but the polymeric structure of MAO stabilises the intermediates in the catalytic cycle.

Jiang reported investigations into a range of aluminoxanes and the resulting effects on ethene tetramerisation.[80] MAO, modified methylaluminoxane (MMAO), ethylaluminoxane (EAO) and isobutylaluminoxane (*i*-BAO) were tested and it was found that MMAO produced the highest selectivities towards 1-octene of up to 73 %. Selectivities and productivities towards 1-octene depend on the amount of aluminoxane used, where

500 equivalents of MAO gave lower selectivities and productivities than 300 equivalents. EAO and *i*-BAO gave low productivities and selectivities.

Bercaw and co-workers used $[H(Et_2O)_2][B(C_6H_3(CF_3)_2)_4]$ and $Na[B(C_6H_3(CF_3)_2)_4]$ as activators which contain weakly coordinating anions.[5] This is a well defined system compared to catalytic systems using MAO, allowing the formation and isolation of compounds which were analogues of intermediates in the catalytic cycle, shown in Scheme 1.21.

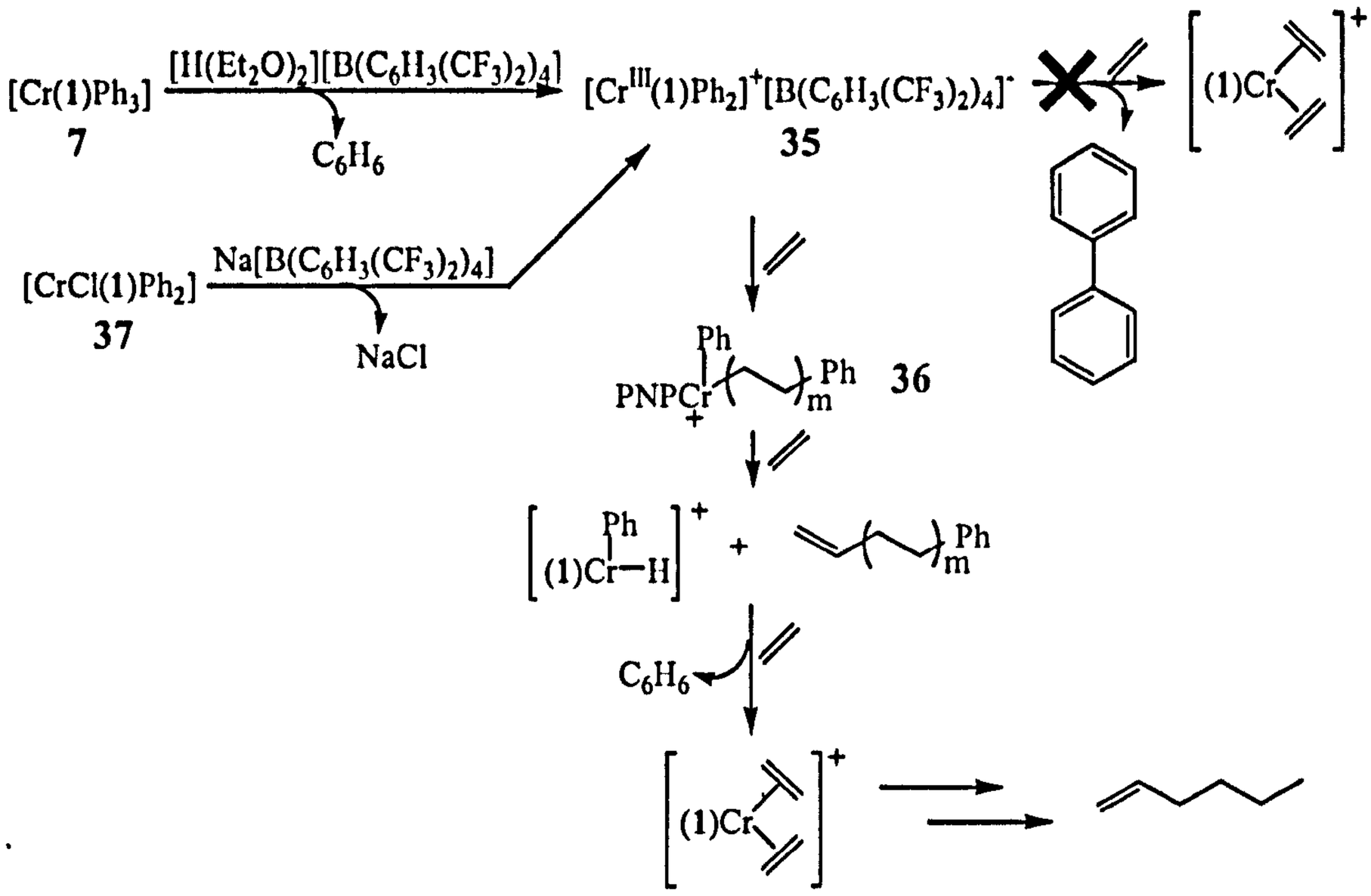


Scheme 1.21 – Activation of CrBr(o,o'-biphenyldiyl) with $NaB[C_6H_3(CF_3)_2]_4$

Activation of compound **33** (Scheme 1.21) with $Na[B(C_6H_3(CF_3)_2)_4]$ generates [CrBr(*o*,*o*'-biphenyldiyl)][$B(C_6H_3(CF_3)_2)_4$], **34**, then on exposure to ethene, the formation of 1-hexene, from ethene trimerisation, is observed by gas-chromatography (GC), along with *o*-vinylbiphenyl. *o*-Vinylbiphenyl is produced from ethene insertion into the biphenyl group, followed by reductive elimination. If **33** is exposed to ethene without prior activation with $NaB[C_6H_3(CF_3)_2]_4$, only *o*-vinylbiphenyl is observed, no 1-hexene is observed. This indicates that activation to form the cationic species is needed for trimerisation to occur.[5]

Bercaw and co-workers also synthesised [$CrPh_3$(**1**)], **7** (see Figure 1.4) which is analogous to [$CrMe_3$(**1**)] species proposed in Scheme 1.22.[5, 39, 40] On activation with

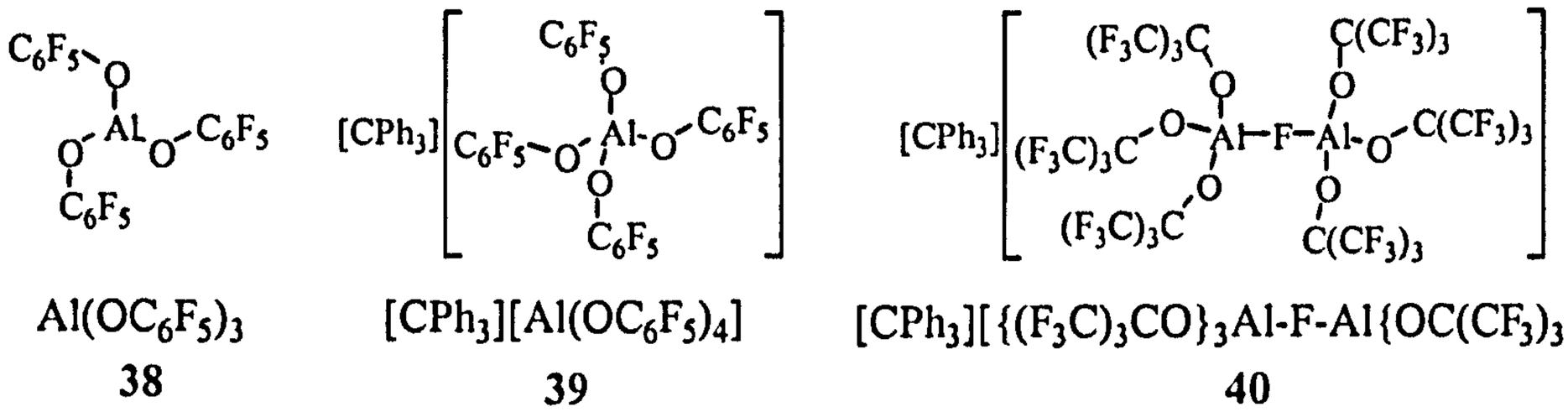
$[H(Et_2O)_2][B(C_6H_3(CF_3)_2)_4]$, trimerisation is observed with productivities and selectivities comparable to the $[CrCl_3(thf)_3]$/1/MAO system developed by Wass and co-workers (Section 1.2.1.3).



Scheme 1.22 – Activation of $[CrPh_3(1)]$ and $[CrClPh_2(1)]$

When $[CrPh_3(1)]$, **7** and $[CrClPh_2(1)]$, **37**, are activated with $[H(Et_2O)_2][B(C_6H_3(CF_3)_2)_4]$ and $NaB[C_6H_3(CF_3)_2]_4$ respectively, $[Cr^{III}Ph_2(1)][B(C_6H_3(CF_3)_2)_4]$, **37**, is formed (Scheme 1.22). It was initially hypothesised that on exposure to ethene, reductive elimination occurs, releasing biphenyl and thus forming the active catalyst, although only trace amounts of biphenyl are observed. Evidence for the formation of styrene and other phenyl containing compounds suggests an activation route where chromium-phenyl bonds are cleaved by the insertion of ethene, followed by β–hydrogen elimination and reductive elimination. Complexes **7** and **37** react with ethene, without activation, to give styrene, ethyl benzene, 4-phenyl-1-butene, benzene and higher ethene-phenyl insertion products. There was no evidence of 1-hexene observed, suggesting that the formation of the Cr cation is needed for trimerisation to occur.

One disadvantage of the MAO system is that this reagent is very expensive and a large excess is needed, this has economic implications when converted to large scale production. A cocatalyst/AlR_3 system could be a cheaper route, leading McGuinness and co-workers to carry out further research on a variety of possible cocatalysts and how the choice of cocatalyst affects selectivity and activity to 1-hexene.[50, 81] Initial investigations have shown that a system using $B(C_6F_5)_3/AlR_3$ or $[Ph_3C][B(C_6F_5)_4]/AlR_3$ along with $[CrCl_3(thf)_3]$ and the PNP ligand, showed high selectivities towards α-alkenes within the C_6 or C_8 fraction but productivities were low compared to the equivalent MAO system and the catalyst underwent rapid deactivation. This lead to investigations into alternative cocatalysts, with weakly coordinating anions. A series of chemically robust and weakly coordinating aluminium cocatalysts with bulky fluorinated alkoxy groups were investigated.[81] A selection of cocatalysts are shown in Figure 1.14. The system used to test the cocatalysts used $[CrCl_3(thf)_3]$ and ligand **19**.



$Al(OC_6F_5)_3$ **38**

$[CPh_3][Al(OC_6F_5)_4]$ **39**

$[CPh_3][\{(F_3C)_3CO\}_3Al\text{-}F\text{-}Al\{OC(CF_3)_3\}]$ **40**

Figure 1.14 – Examples of Aluminium Fluorinate Cocatalysts

Table 1.16 – Ethene Oligomerisation using the Aluminate Cocatalysts in Figure 1.14.

Reaction	Cocatalyst	$AlEt_3$ Equivalents	Productivity / g (g Cr h)$^{-1}$	Product Distribution			
				C_6	1-C_6[b]	C_8	1-C_8[c]
1.52[a]	**38** (1.3 eq)	30	5,810	85.2	98.5	3.9	94.6
1.53	**39** (1.5 eq)	100	125,600	16.3	68.9	72.2	99.0
1.54	**40** (3.0 eq)	100	53,120	18.6	76.3	68.2	99.4

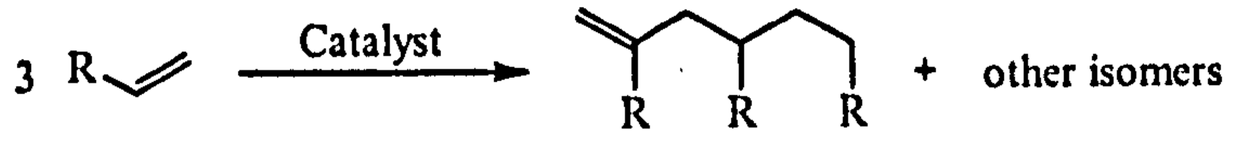
0.01 mmol $[CrCl_3(thf)_3]$, 0.012 mmol **19**, toluene, 45 °C, 40 bar ethene; [a] 0.03 mmol $[CrCl_3(thf)_3]$, 0.036 mmol **19**; [b] Selectivity within C_6 fraction; [c] Selectivity within C_8 fraction;

Table 1.16 shows the results obtained from systems using the aluminate cocatalysts shown in Figure 1.14. In reaction 1.38 in Table 1.12 the system using **19** with $[CrCl_3(thf)_3]$ and MAO, shows a selectivity to C_8 of 68.3 % of which 98.9 % is 1-C_8. In reaction 1.52 in Table 1.16 it can be seen that using **38** as the cocatalyst along with $AlEt_3$ causes the system to become selective towards C_6 (85.2 %) and the productivity is reduced to 5,810 g (g Cr h)$^{-1}$. The catalyst experiences rapid deactivation, resulting in a low productivity. It is suggested that the reason for this switch in selectivity is due to the formation of a more coordinating anion $[AlEt(OC_6F_5)_3]^-$ and the coordination of this anion mimics the pendant donation of the OMe group in **1** (se Figure 1.2). From this it was thought that the C_6/C_8 selectivity can be controlled by the strength of the anion coordination.

The system using aluminate **39** (reaction 1.53 in Table 1.16) gave a productivity of 125,600 g (g Cr h)$^{-1}$, with a selectivity to C_8 of 72.2 %, of which 99.0 % was 1-C_8. As with aluminate **38**, the system using **39** (reaction 1.4 in Table 1.16) experiences deactivation at high equivalents of $AlEt_3$. **40** gave a lower productivity than **39** and the productivity and selectivity of the system was also influenced by the amount of aluminate added, with the highest productivity achieved with three molar equivalents of aluminate. A series of degradation studies were carried out and it was found that the system begins as a tetramerisation system then converts to a trimerisation system, showing that the cocatalyst is changing over time and anion coordination strength increases as the reaction occurs. The degradation may be due to an equilibrium, where the chromium centre is activated with $AlEt_3$ to give a Cr-Et species which then reacts with the aluminate, giving for example a Cr-$AlEt_3(OC_6F_5)$ species (for aluminate **38**).[80] These system provide a cheaper alternative to MAO, giving comparable productivities and selectivities to C_6 or C_8.

1.5. Trimerisation of Other α-alkenes

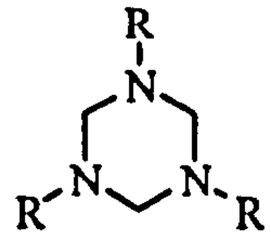
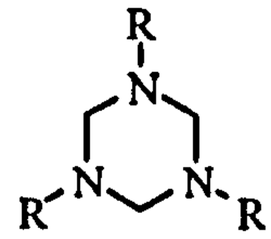
As stated in Section 1.2.1.2, Köhn found that it was possible to trimerise higher α-alkenes using 1,3,5-triazacyclohexane ligands.[22]



Scheme 1.23 – Trimerisation of Higher a-Alkenes

Using 1,3,5-triazacyclohexane ligands with $[CrCl_3(thf)_3]$ and MAO as an activator, a conversion of 80 % was achieved, as shown in Table 1.17.

Table 1.17 – Trimerisation of Higher α-Alkenes

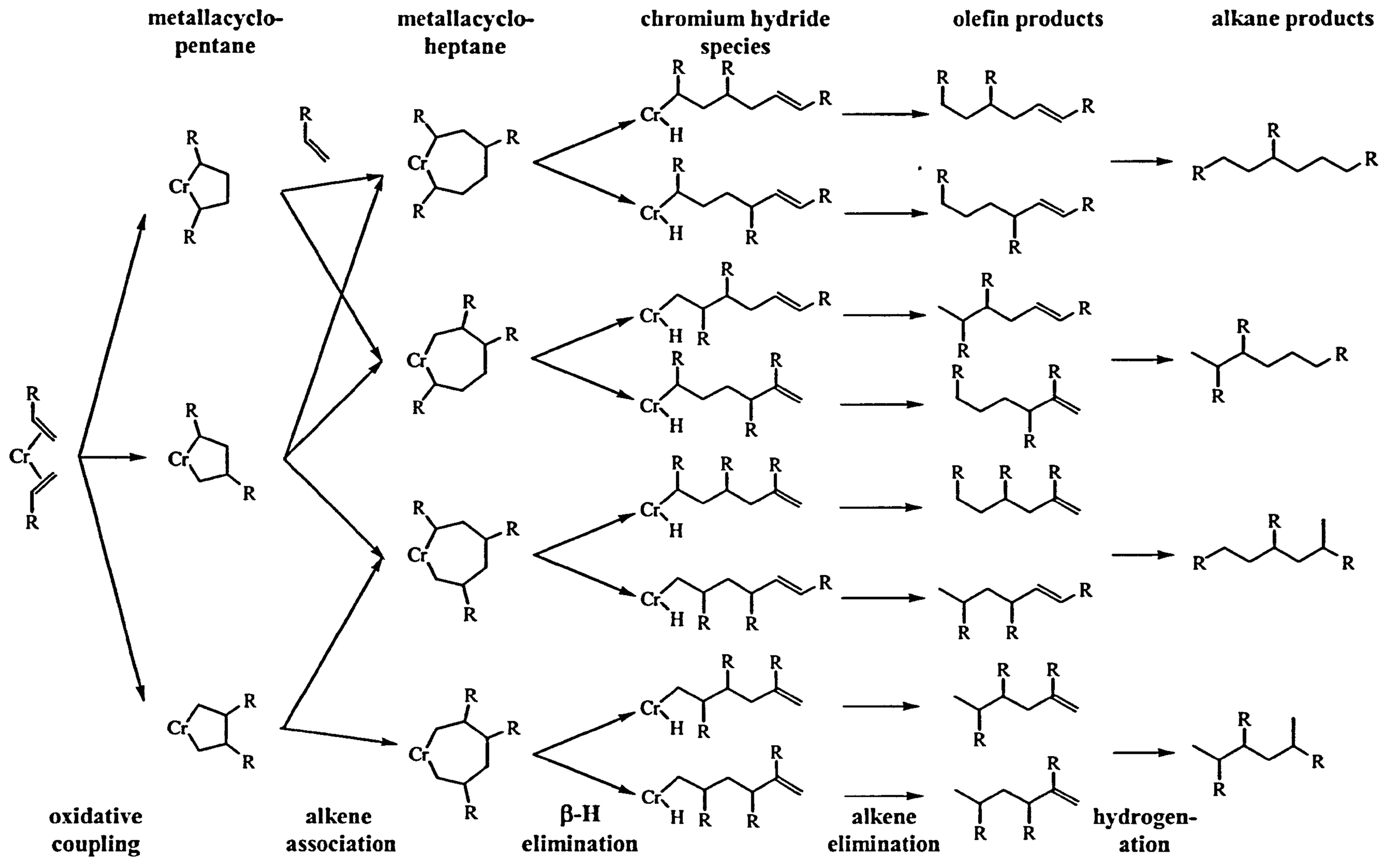
Reaction	Ligand	Precatalyst	Activator and Solvent	Conditions	Productivity, Selectivity to Alkene
1.55	 R = 2-ethylhexyl	$[CrCl_3(thf)_3]$	MAO, 1-dodecene	0 °C, 20 h	166 g (g Cr h)$^{-1}$, C_{36} – 93.0 % Internal C_{12} – 7 %
1.56	 R = dodecyl	$[CrCl_3(thf)_3]$	MAO, 1-dodecene	0 °C, 20 h	117 g (g Cr h)$^{-1}$, C_{36} – 81.0 % Internal C_{12} – 19 %

Wasserscheid and co-workers used 1,3,5-triazacyclohexane ligands to trimerise 1-decene and 1-dodecene. The hydrogenated C_{30} and C_{36} trimer products were found to be useful for synthetic lubricants. Trimerisation of 1-dodecene was carried out using 100 equivalents of MAO, in toluene, at 0 °C for 20 hours. The ligand that gave the best results in shown in reaction 1.55 in Table 1.17, is *N,N,N*-tri-2-ethylhexyltriazacyclohexane, which gave a productivity of 166 g (g Cr h)$^{-1}$, with a selectivity to C_{36} of 93 % and 7 % internal C_{12} compounds, from the isomerisation of 1-dodecene. Although the productivity is low, the selectivity is high and this is one of

the first systems to trimerise higher alkenes. The selectivity and productivity were affected by the degree of branching of the R group on the nitrogen of the ligand, a more bulky but less branched R group decreased the selectivity and productivity. For example when R is dodecyl group (reaction 1.56 in Table 1.17) the selectivity to C_{36} is 81.0 % and productivity was only 117 g (g Cr h)$^{-1}$.[2, 82]

The products are formed *via* the metallacycle mechanism, forming internal alkenes and vinylidenes. The product mixture contained four main products after hydrogenation and there was no evidence of α-alkenes formation. Scheme 1.24 shows that mechanism by which the trimerisation of higher α-alkenes occurs, where four alkane isomers are formed after hydrogenation.[82] This scheme follows the metallacycle mechanism described in Scheme 1.13, but is more complicated due to the ability of α-alkenes to bind to the metal centre *via* 1,2 or 2,1 insertion, leading to three different metallacyclopentane intermediates. The insertion of the third α-alkenes can again insert either *via* 1,2 or 2,1 insertion, giving four unique metallacycloheptane intermediates. After β-hydride elimination and reductive elimination occurs, eight different alkene isomers are produced, consisting of internal alkenes and vinylenes, as seen in the Wasserscheid 1,3,5-triazcyclohexane systems.

The system was unable to trimerise conjugated alkenes or internal alkenes. In addition the successful ligands had bulky long chain alkyl group in the R position, if R is a methyl group the catalyst is inactive towards trimerisation of higher α-alkenes.[22]



Scheme 1.24 - Formation of Isomers in Trimerisation of Higher α-Olefins

1.6. Aims and Objectives

The work presented in this thesis investigates further uses of chromium PNP complexes in the trimerisation of substituted α-alkenes. The system based on that developed by Wass and co-workers will be employed, with $[CrCl_3(thf)_3]$, a PNP ligand and MAO.[4] This system will be used to investigate:

- Cotrimerisation of ethene with substituted alkenes, such as styrene, cyclohexane, norbornene, maleic anhydride, methyl methacrylate and acrylonitrile. The products formed from successful cotrimerisation will be identified *via* comparison with standard compounds and NMR spectroscopy.
- Homotrimerisation of 1,3-dienes, such as isoprene, 1,3-butadiene and 2,3-dimethyl-1,3-butadiene. The trimerisation of isoprene is of potential interest, the products being terpenoids.
- The activity and selectivity of novel PNP ligands, with oxygen donating substituents on the *ortho* position of the phenyl rings, for ethene trimerisation/tetramerisation.

As described the $[CrCl_3(thf)_3]$/**1**/MAO system is usually activated by methylation of the chromium precursor and the reduction of the Cr(III) centre to Cr(I). Investigations were carried out into an alternative activation method, by starting with a Cr(0) centre and oxidising to Cr(I) upon activation. A series of chromium (0) carbonyl PNP complexes were synthesised and tested for ethene trimerisation by this route.

1.7. Summary

Ethene trimerisation and tetramerisation are selective methods of synthesising 1-hexene and 1-octene respectively from ethene, which are used in the synthesis of linear low density polyethylene (LLDPE). A wide range of research, industrial and academic, has been carried out in this field due to these industrial applications. This chapter has reviewed the range of chromium systems which have been tested for ethene trimerisation, as well as a small selection of other metals. Chromium PNP systems have been shown to be highly active and selective towards ethene trimerisation, with one of the best systems being developed by Wass and co-workers, using $[CrCl_3(thf)_3]$, **1** and

MAO. Under 20 bar of ethene and at 80 °C, this system gave a productivity of 1,033,000 g (g Cr h)$^{-1}$ and a selectivity towards 1-hexene, within the hexene fraction of 99.8 %, this system also gave high productivities at 1 bar of ethene and room temperature. Cr PNP systems have also been shown to selectively tetramerise ethene to 1-octene. One of the best systems with respect to selectivity uses **19** as the ligand, giving a productivity of 272,400 g (g Cr h)$^{-1}$ and a selectivity of 68.3 % towards octene of which 98.9 % is 1 octene. The system using ligand **28** gave one of the highest productivities of 2,279,200 g (g Cr h)$^{-1}$, with a selectivity to C_8 of 63.7 %, of which 99.5 % is 1-C_8.

The mechanism for ethene trimerisation proceeds *via* a metallacycle route, where two ethene molecules coordinate to the metal centre and oxidatively couple to give a metallacyclopentane, this is followed by further ethene insertion to give a metallacycloheptane and β-hydride elimination and reductive elimination to give 1-hexene. This mechanism is then extended to take into account the discovery of ethene tetramerisation. A wide range borate and aluminate activators have been investigated to replace MAO, where it was found that a large non-coordinating anion is needed. This thesis investigates the use of Cr PNP systems for trimerisation and cotrimerisation of other α-alkenes and alternative routes into the activation of the chromium centre for ethene trimerisation.

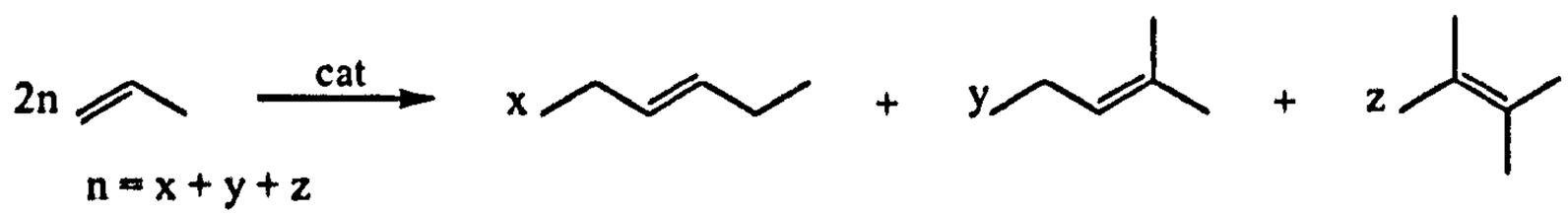
Chapter 2

Cotrimerisation of Ethene with Styrenic Monomers

2.1. Introduction

2.1.1. Codimerisation of Alkenes

Homodimerisation and codimerisation of alkenes are important methods for synthesising higher alkenes and are widely used in industry. For example, the homodimerisation of propene has been extensively researched using a wide range of metals, a general system is shown in Scheme 2.1.[83, 84]



Scheme 2.1 – Homodimerisation of Propene

Common catalysts are η^3-allylnickel species with triaryl- or trialkyl-phosphines that are activated by Lewis acids such as $AlCl_2Et$. In 1965 Wilke and co-workers developed the η^3-allylnickel complex shown in Figure 2.1.[84]

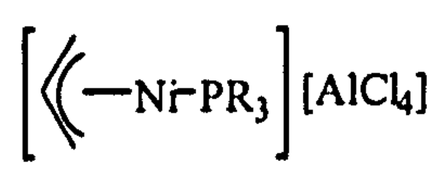
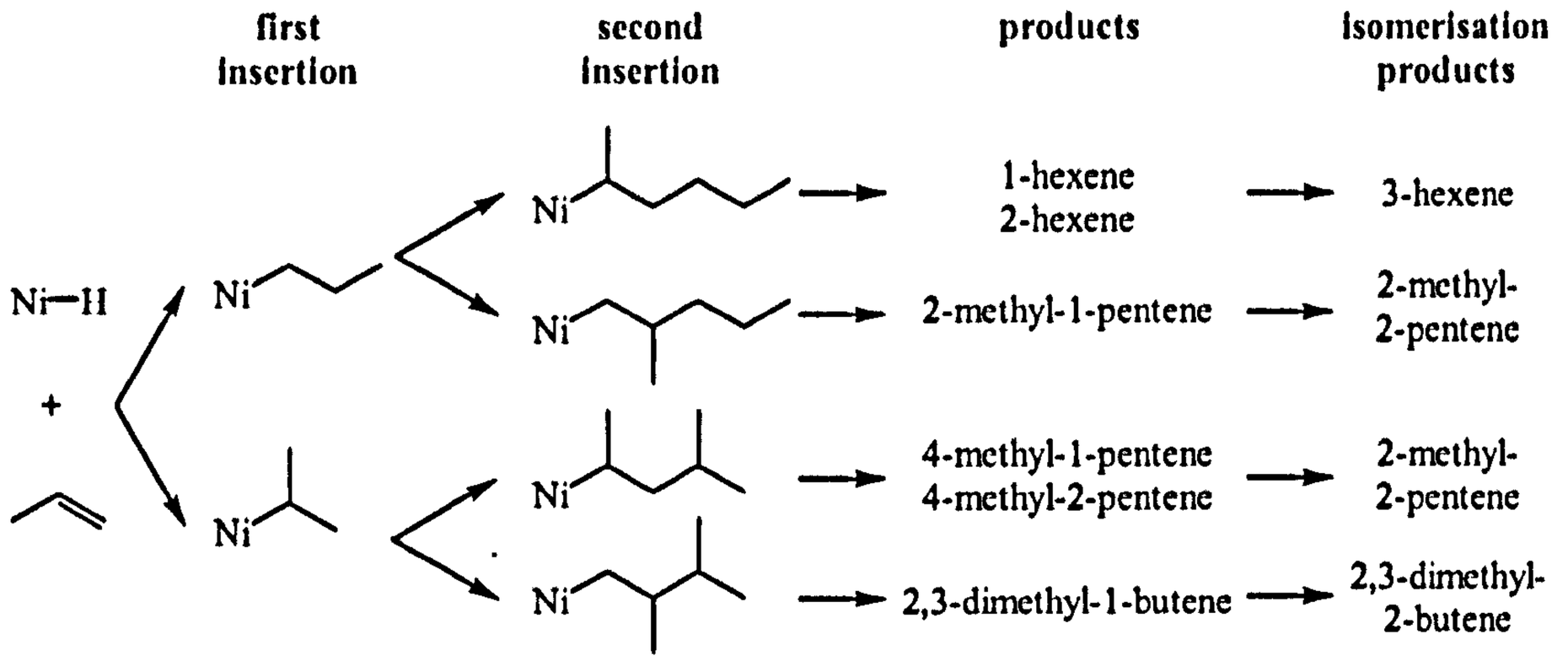


Figure 2.1 – η^3-Allylnickel Complex Developed by Wilke and Co-workers

The group found that the tertiary phosphine has an effect on the regioselectivity of the products, with sterically demanding phosphines favouring the formation of 2,3-dimethylbutene. Codimerisation occurs *via* an insertion/elimination mechanism, an example of which is shown in Scheme 2.2.[85]



Scheme 2.2 – Dimerisation of Propene by Nickel Complexes

The η^3-allylnickel species undergoes insertion of propene and then β-hydride elimination to give the active nickel hydride species. The catalytic cycle then goes *via* insertions of propene into the nickel hydride species, followed by a β-hydride elimination to give the products and reforming the nickel hydride species. The catalyst can isomerise the products to thermodynamically stable alkenes, giving a more complex mixture of products.[84, 85] The systems are often very productive, for example [Ni(η^3-C_3H_5)(PR_3)][$AlR'X_3$], where R is a bulky alkyl group, gives turnover frequencies of over 625,000 h^{-1}.[3]

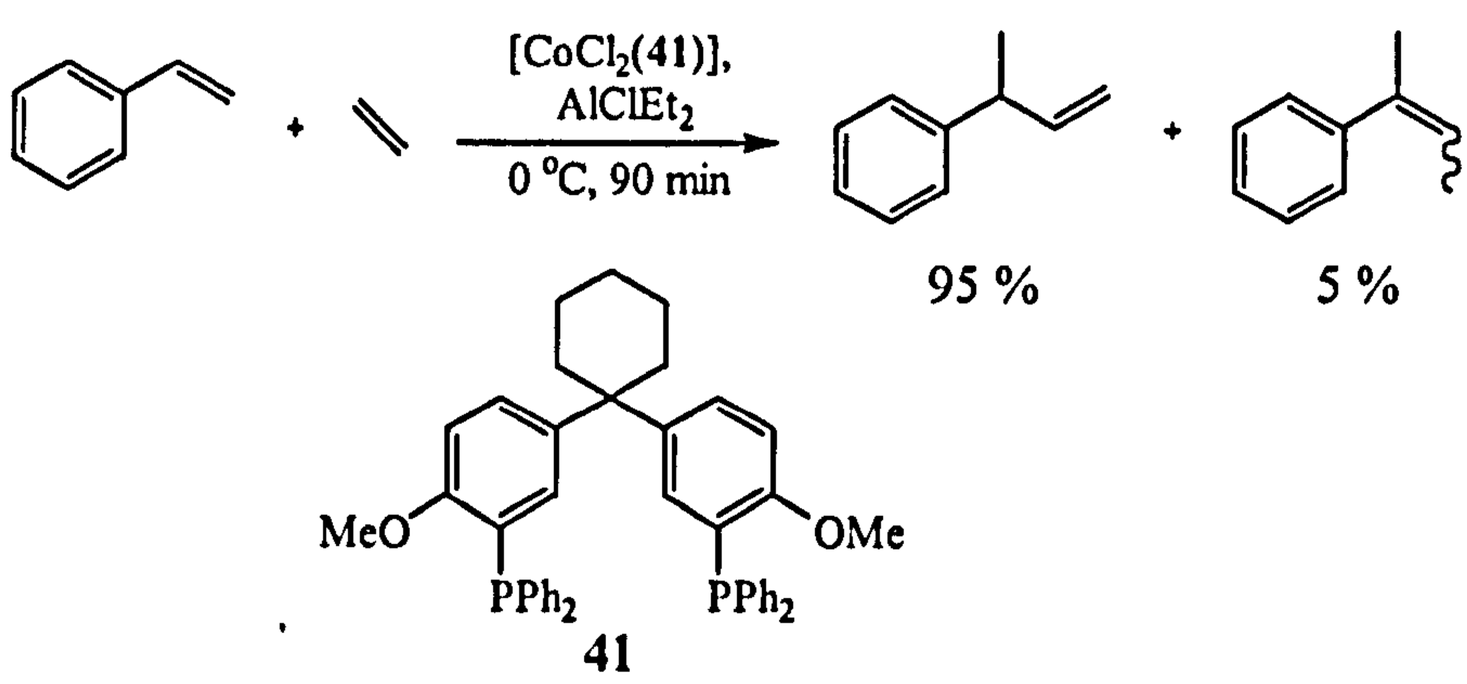
Codimerisation reactions (i.e. two different monomers) are more difficult. Ziegler developed a system for the codimerisation of ethene and butene using titanium tetrabutyl ester and trialkylaluminium.[84] The catalytic cycle involves the formation of metallacyclopentane, which is similar to the chromium metallacyclopentane formed in the trimerisation of ethene (Section 1.2.3). The dimerisation of ethene to give butene is also observed.

Codimerisation of ethene and styrene was first reported in 1965, using rhodium chloride as the catalyst. Under 1000 atmospheres of ethene and 2 g of catalyst, 2-phenyl-2-butene was produced. This research also extended to the codimerisation of ethene with other alkenes. A wide range of nickel and palladium catalyst systems were subsequently developed such as [Ni(acac)$_2$]/dppe/$Al_2Cl_{6-y}Et_y$, (acac = acetylacetonate),[86] and [Pd(C_4H_7)Cl(Ph_2PCH_2COOEt)].[87] From these systems the major products are initially 3-aryl-1-butenes but isomerisation can occur giving a mixture of the *E* and *Z*

isomers of 2-aryl-2-butenes, known as head-to-tail isomers.[84, 85] The observed products imply that styrene inserts *via* a 2,1 regiochemistry.

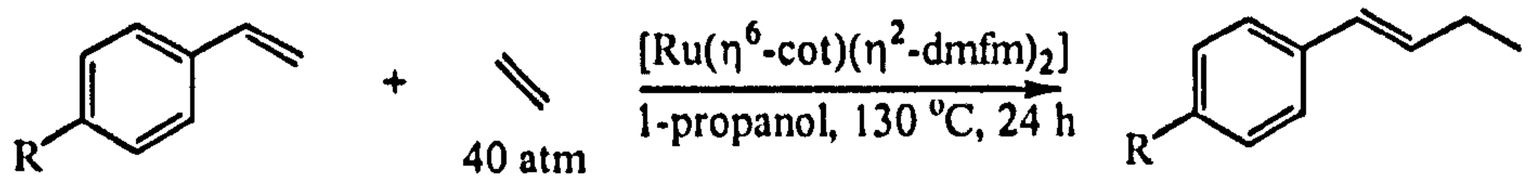
The compounds formed *via* codimerisation can have a chiral centre, this has lead to the development of catalysts for asymmetric codimerisation or hydrovinylation, two examples are given in Scheme 2.3 and Scheme 2.4.[3] In many systems, isomerisation of the products is still observed; therefore it is a valuable objective to develop a catalyst which minimises this isomerisation.

In 2005 Grutters and co-workers developed a cobalt system using diphosphine ligands for asymmetric codimerisation (hydrovinylation) of styrene and ethene, with a high selectivity towards 3-phenylbut-1-ene.[88] The best results came from a system shown in Scheme 2.3, using 5 equivalents of $AlClEt_2$, 0.001 mol % of catalyst and 30 bar of ethene, at 0 °C for 90 min. A conversion of 100 % was achieved with a selectivity to codimer products of >99 % and a selectivity of 95 % to 3-phenyl-1-butene.



Scheme 2.3 – Codimerisation of Styrene and Ethene Using a Cobalt System

More recently Kondo and co-workers developed a zero-valent ruthenium catalyst which, in the presence of an alcohol, was capable of forming (*E*)-1-aryl-1-butenes (head to head isomer), with a 80 % yield and a selectivity of 95 % to the isomer shown in Scheme 2.4 where R is hydrogen, as shown in Scheme 2.4.[89]



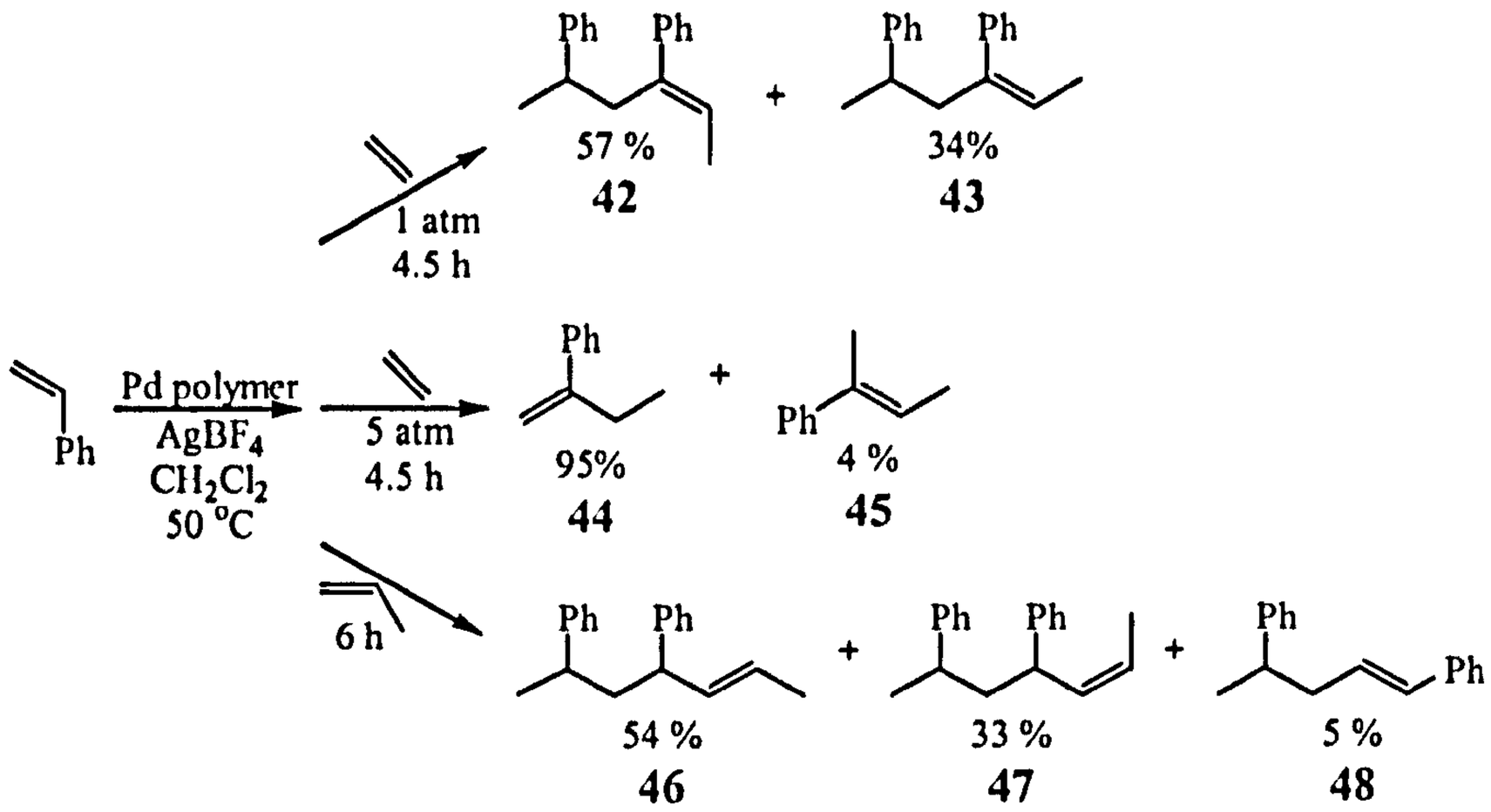
Scheme 2.4 – Codimerisation of Styrene and Ethene

It is noteworthy that although these codimerisation systems often achieve good selectivity, with the exception of Ziegler titanium based catalysts, they operate *via* a simple insertion/elimination mechanism.

2.1.2. Background to Cotrimerisation

Cotrimerisation is a method of forming functionalised terminal alkenes, which can be used in a variety of applications including comonomers for polymerisation, giving polymers with improved functionality, such as better printability and wettability. Current organic routes to these ω-substituted alkenes can be long and difficult, whereas cotrimerisation is a simple, one step route to these compounds. Extensive research has been performed in the area of ethene trimerisation and the codimerisation of ethene with other alkenes, due to the many industrial applications but very little research has been conducted into the related area of cotrimerisation.

In 1977 Kaneda and co-workers developed a heterogeneous catalytic system using palladium (II) chloride on a polystyrene resin, with silver tetrafluoroborate, $AgBF_4$, as a cocatalyst.[90] It was shown that this system could cotrimerise styrene and ethene to give diphenylhexene, consisting of two styrene molecules and one ethene molecule. This system has a 100 % conversion of styrene to cotrimer or dimer products under one atmosphere of ethene. The products formed by various conditions are shown in Scheme 2.5.



Scheme 2.5 – Cotrimerisation of Styrene and Ethene Using Pd Polymer[77]

At 5 atmospheres of ethene the system switches to dimerisation of ethene and styrene, giving compounds **44** and **45**. It was also found that the Pd polymer system could cotrimerise styrene with propene giving a selectivity to trimer **46** of 54 %. Homodimerisation of styrene also occurs in the absence of ethene to give 90 % compound **48** after 1 h. Dimerisation of ethene or propene was observed but had a low conversion at atmospheric pressure of propene.

Pellecchia and co-workers found that the copolymerisation of styrene and ethene using a $[TiCp^*Me_3][B(C_6F_5)_3]$ system ($Cp^* = \eta^5\text{-}C_5Me_5$), produced a polymer with a polyethylene backbone and 4-phenylbutyl branches.[91] It was concluded that the 4-phenylbutyl branches were produced from the incorporation of 6-phenyl-1-hexene into the polymer chain and that this isomer was produced by the cotrimerisation of ethene and styrene. Under suitable conditions the polymer contained 52 - 54 mol % of phenylbutyl branches (Figure 2.2). It was proposed that there are several different Ti species in solution, some able to copolymerise 6-phenyl-1-hexene with ethene, some able to cotrimerise styrene with ethene and some able to polymerise ethene.

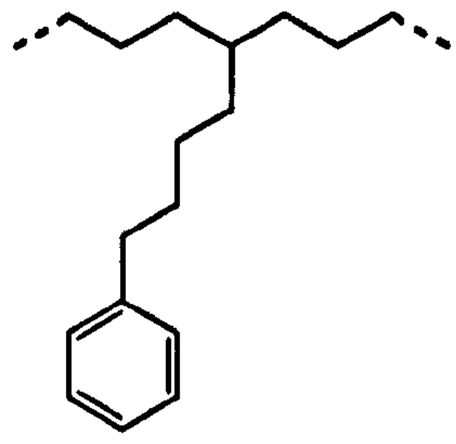


Figure 2.2 - 4-Phenylbutyl Branched Polyethylene

Further research into the cotrimerisation of ethene and styrene by this group reported a half titanocene catalyst to cotrimerise ethene and styrene, giving phenylhexene.[92] The system which gave the largest cotrimer fraction was $[Ti(\eta^5\text{-}C_5H_5)Cl_3]$, with 5.2 mmol of methylaluminoxane (MAO) in toluene at 20 °C and under 1 bar of ethene. The various systems produced between five and six cotrimers depending on the system. The cotrimers were analysed by gas chromatography (GC). Figure 2.3 shows a selection of the cotrimers produced by this system. Polyethylene and polystyrene were also produced.

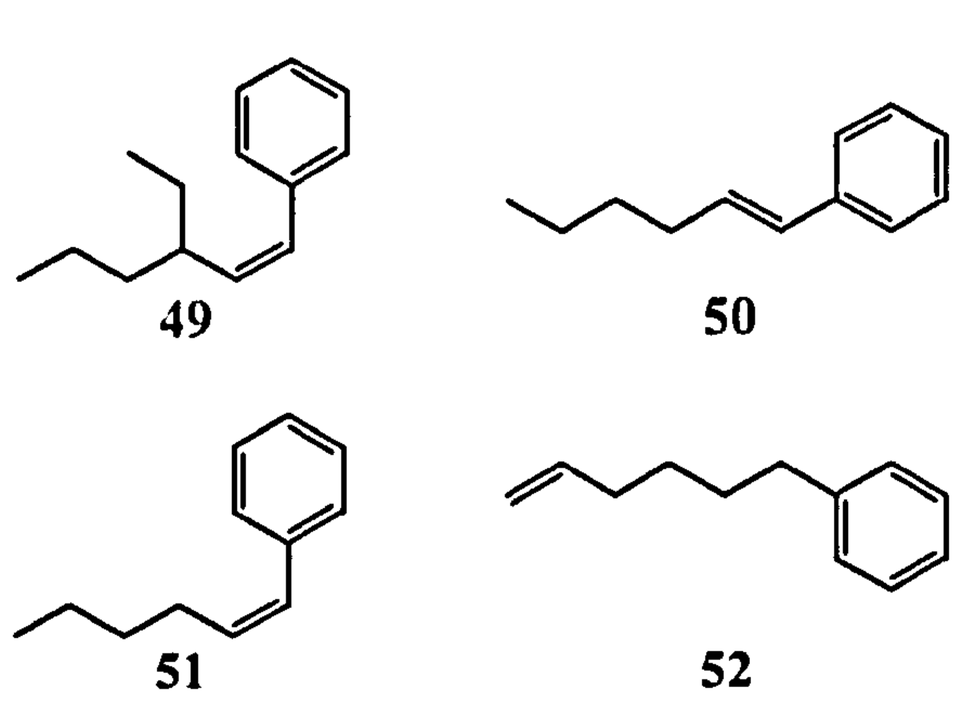


Figure 2.3 – Products from Cotrimerisation of Styrene and Ethene

There have been other examples of cotrimerisation, for example the production of C_{10+} compounds in ethene trimerisation shows that 1-hexene has been incorporated into the trimer.[4] Also Wass and co-workers added butene to a trimerisation experiment using the catalyst in Scheme 2.6, $[CrCl_3(thf)_3]$, **1** and MAO system increasing the amount of C_8 materials produced from the cotrimerisation of 1-butene and ethene.

2.2. Cotrimerisation of Ethene with Alkenes

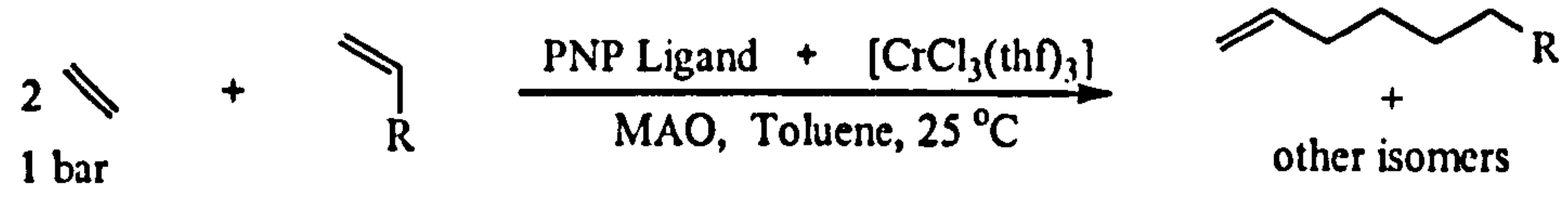
2.2.1. Objectives

The aim of this research was to investigate cotrimerisation of functionalised alkenes and ethene, utilising a catalytic system using *N,N*-bis(diarylphosphino)amine (PNP) ligands, a chromium precursor, $[CrCl_3(thf)_3]$ and MAO.[1, 4, 5] The research was also extended to include bis(diarylphosphino)methane and bis(diarylphosphino)ethane ligands derivatives. Chromium PNP systems have been shown to be highly active and selective towards ethene trimerisation and tetramerisation. Therefore it was hypothesised that the catalytic ability of these systems could be extended to the cotrimerisation of ethene with other alkenes.[1, 4, 5, 36, 37, 41, 47]

Ethene trimerisation with Cr catalysts goes *via* a metallacycle mechanism (Section 1.2.3). It was suggested that cotrimerisation could occur *via* the same route. This may reduce the chance of isomerisation occurring, like with the Ni, Pd and Ru systems described in section 2.1.1. Also unlike these systems, the chromium-based catalysts operating by a metallacycle mechanism, should give excellent selectivity to trimerisation products.

2.2.2. Methodology

The general cotrimerisation reaction is shown in Scheme 2.6.[1, 4, 5]



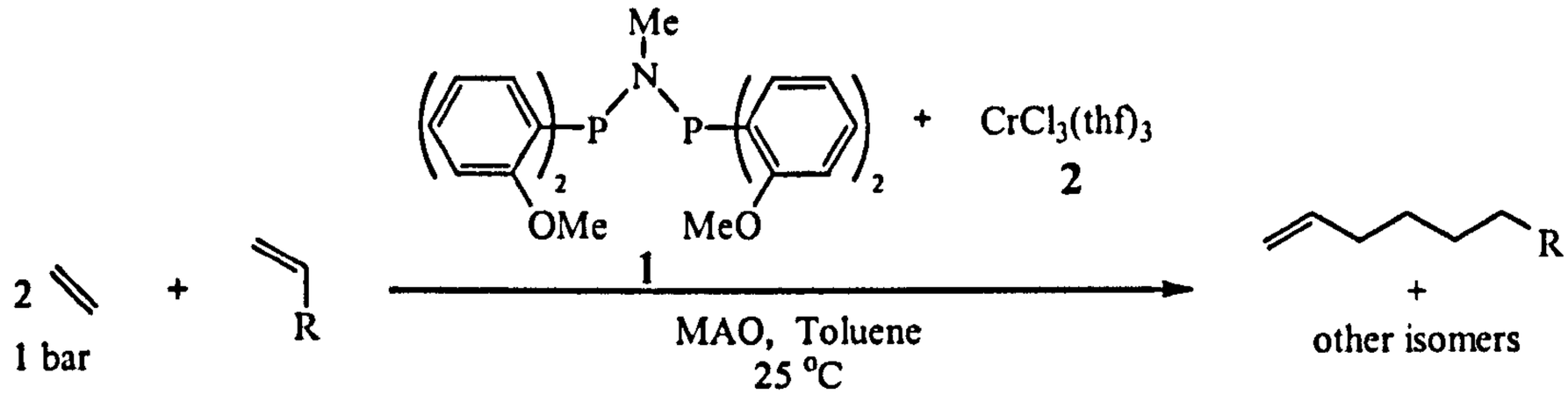
Scheme 2.6 – General Method for Cotrimerisation

$[CrCl_3(thf)_3]$ was used as the catalyst precursor, with a PNP ligand and MAO was used as the cocatalyst. Unless otherwise stated, each run was performed at room temperature. The total volume of the reaction mixture was kept constant, so the volume of toluene added depended on the volume of the comonomer added. A low ethene

pressure of 1 bar was used to increase the potential for the incorporation of the functionalised alkene into the catalytic cycle and maximise the cotrimer to 1-hexene (i.e. ethene homotrimerisation) ratio.[93]

2.3. Cotrimerisation of a Range of Substituted Alkenes with Ethene

The first system chosen, $[CrCl_3(thf)_3]$/1/MAO, is shown in Scheme 2.7. This system is one of the best reported for the trimerisation ethene to 1-hexene, producing a productivity of 1,033,200 g (g Cr h)$^{-1}$, with an overall selectivity to 1-hexene of 89.9 %.[1, 4, 5]



Scheme 2.7 – $[CrCl_3(thf)_3]$/1/MAO System

The cotrimerisation of ethene with various functionalised alkene comonomers was investigated. Results from a series of catalytic runs using cyclopentene, norbornene, maleic anhydride, methyl methacrylate, methyl acrylate, acrylonitrile, ethyl vinyl ether or styrene as the comonomer are shown in Table 2.1. The concentration of the comonomer is shown in the table and the amount of toluene used depended on the amount of comonomer added, with a total volume of 44 mL. Run 2.1 shows the data obtained for a reaction with only ethene, with a productivity of 8654 g (g Cr h)$^{-1}$ and a selectivity to C_6 of 91.5 %, this is in line with literature values at this pressure.[4] The general reaction conditions used in Table 2.1 are 0.02 mmol $[CrCl_3(thf)_3]$, 0.02 mmol ligand **1**, 300 molar equivalents of MAO cocatalyst, toluene, a temperature of 25 °C, 1 bar ethene and a reaction time of 1 hour. The productivity was found from mass gain, using the same equation as shown in Section 2.4.1.3 and the selectivity was determined from the GC data.

Table 2.1 – Cotrimerisation of Functionalised Alkenes with Ethene

Run	Comonomer	Comonomer Concentration / mol dm^{-3}	Productivity / g (g Cr h)$^{-1}$	Selectivity (wt %)				
				Co-Trimers	C_6	1-C_6[a]	C_{10}	C_{14}
2.1	None	-	8654	-	91.5	86.1	7.0	1.5
2.2[b]	Cyclopentene	0.5	1212	0.0	75.2	96.0	10.2	0.0
2.3	Cyclopentene	1.3	269	0.0	99.5	97.0	0.5	0.0
2.4[c]	Cyclopentene	6.7	1173	0.0	100.0	99.8	0.0	0.0
2.5	Norbornene	7.4×10^{-4}	6192	0.0	60.8	96.7	34.5	4.7
2.6	Norbornene	6.0	0	0.0	0.0	0.0	0.0	0.0
2.7	Maleic Anhydride	5.3×10^{-4}	1951	0.0	92.0	99.6	8.0	0.0
2.8	Maleic Anhydride	0.2	673	Too many peaks for analysis				
2.9	Methyl Methacrylate	0.4	721	Polymer Formed – No Cotrimer				
2.10	Methyl Methacrylate	6.4	320	Polymer Formed – No Cotrimer				
2.11[d]	Methyl Methacrylate	3.8	0	Polymer Formed – No Cotrimer				
2.12	Methyl Acrylate	0.4	404	Polymer Formed – No Cotrimer				
2.13[d]	Methyl Acrylate	7.6	0	Polymer Formed – No Cotrimer				
2.14	Ethyl Vinyl Ether	7.1	0	No product formed				
2.15	Acrylonitrile	10.4	0	No product formed				
2.16	Styrene	6.0	7926	95.8	4.18	-	0.0	0.0

[a] within C_6 fraction, [b] 2 h run time, [c] 6h run time, [d] 70 °C.

In runs 2.2 – 2.4, cyclopentene is not incorporated into the products and so only C_6 and C_{10} alkenes are formed from the trimerisation of ethene and incorporation of 1-hexene into the trimerisation mechanism. Incorporation still is not observed at 70 °C. It can be

seen that as the concentration of cyclopentene is increased, the selectivity to C_6 materials and 1-hexene in particular increases. The possibility of the incorporation of 1-hexene into the catalytic mechanism may be reduced due to the higher solubility of ethene in cyclopentene over toluene and the lower concentration of 1-hexene due to a lower productivity. Both of these factors may contribute to the lower percentage of C_{10} and C_{14} materials and the higher selectivity towards 1-hexene.

As with cyclopentene the cotrimerisation of norbornene and ethene, run 2.5, was unsuccessful and the only products were C_6, C_{10} and C_{14} products. The productivity is reduced from 8654 g (g Cr h)$^{-1}$ for the ethene run (run 2.1) to 6192 g (g Cr h)$^{-1}$ and C_6 percentage is reduced to 60.8 %, although the selectivity towards 1-hexene, within this fraction, is still 96.7 %. At a high concentration of norbornene, run 2.6, the catalyst was deactivated and no hexene was present. Maleic anhydride again showed similar results to norbornene with the productivity reduced to 1951 g (g Cr h)$^{-1}$ at a low concentration of comonomer, with a C_6 selectivity of 92.0 % and a selectivity of 99.6 % to 1-hexene within the C_6 fraction. In run 2.8, with a high concentration of maleic anhydride the GC trace contained too many peaks for analysis to be completed. Reaction of this substrate with the MAO cocatalyst, leading to degradation products cannot be ruled out.

Runs 2.9 to 2.13 show results using methyl acrylate and methyl methacrylate, where only poly(methylmethacrylate) or poly(methylacrylate) were produced. At low concentrations of methylacrylate or methyl methacrylate, the overall productivity is zero, this may be because these substrates react with MAO, either preventing MAO taking part in the catalytic cycle or deactivating the catalyst. These results suggest that this cocatalyst is not appropriate, when using comonomers containing carbonyl or ether groups. The cotrimerisation of ethyl vinyl ether and acrylonitrile with ethene was also unsuccessful, again reaction of these monomers with MAO is possible.

In conclusion, most comonomers are not incorporated into the catalytic cycle with these catalysts. Activity to 1-hexene is still observed in most cases, albeit at lower activity than in the absence of a comonomer. This suggests that the comonomer is not irreversibly binding to the metal, but the observed poisoning effect is caused by competitive reversible binding of the comonomer. Other comonomers, specifically acrylonitrile and vinyl ethers, shut down catalysis completely. The one comonomer that

did prove successful was styrene which was shown in run 2.16 to produce cotrimer with high selectivity. Further investigations into the results produced by using styrene are described in the next section.

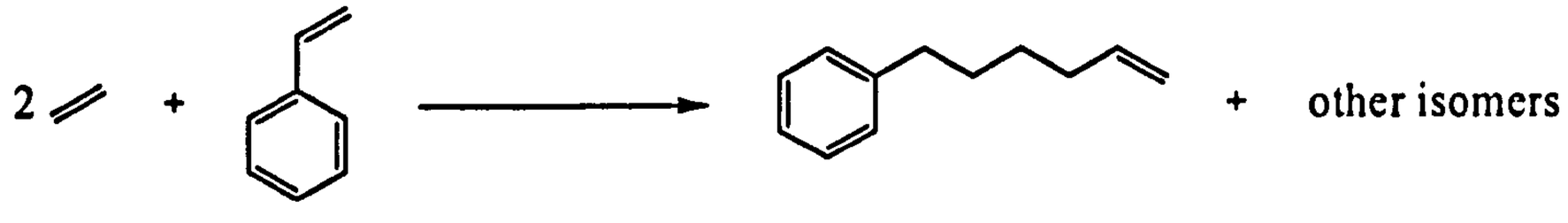
2.4. Cotrimerisation of Styrene and Ethene

2.4.1. $[CrCl_3(thf)_3]$/*N*,*N*-bis(di-*ortho*-methoxyphenylphosphino)methylamine, 1/MAO System

2.4.1.1. Analysis of Cotrimer Products

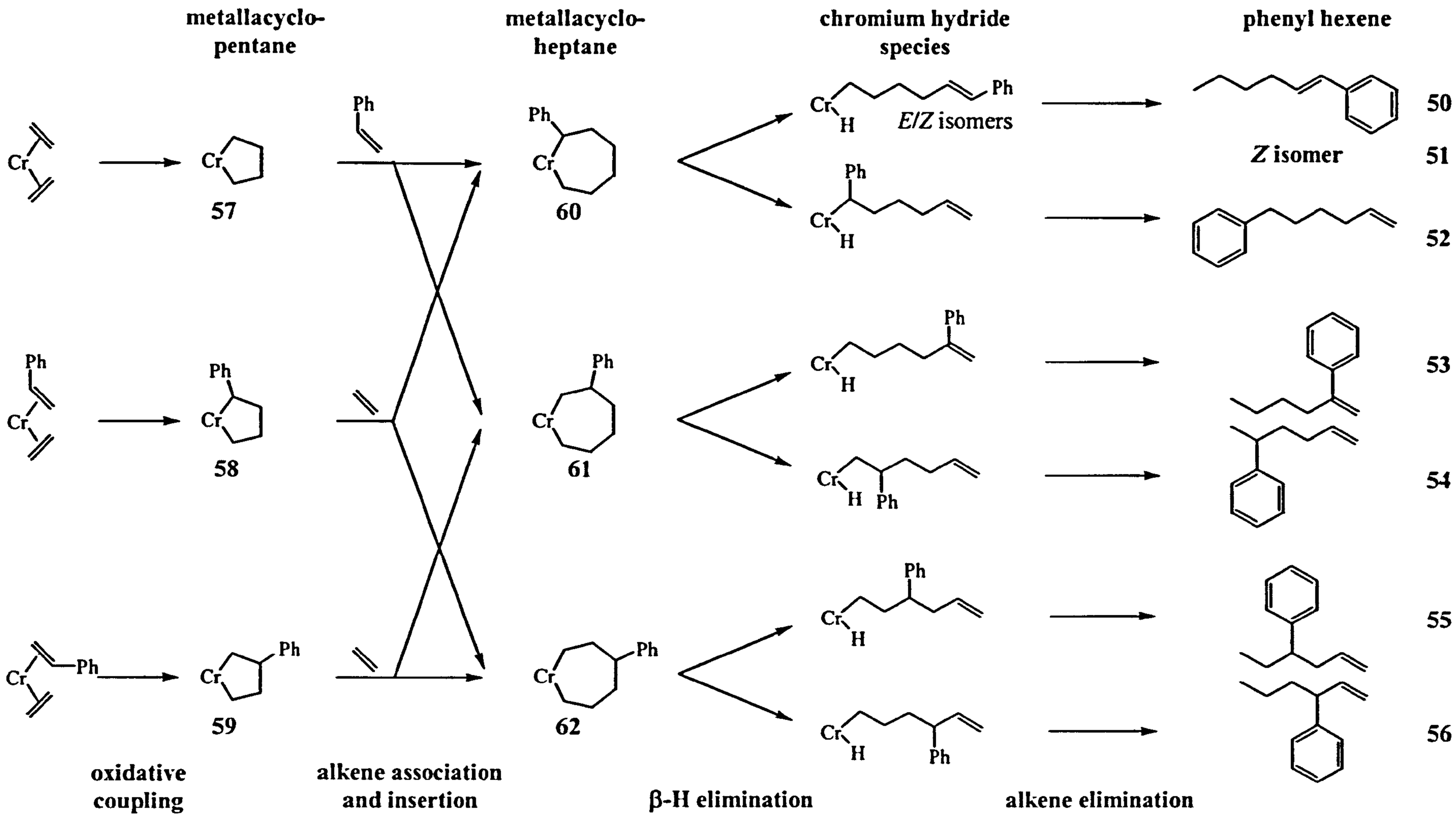
As seen in Run 2.16 in Table 2.1, the cotrimerisation of styrene and ethene was successful. A total productivity of 7924 g (g Cr h)$^{-1}$ was achieved with a styrene concentration of 6.0 mol dm^{-3} and an ethene pressure of 1 bar, using 0.02 mmol of $[CrCl_3(thf)_3]$ and 1 equivalent of ligand **1**. A selectivity of over 95 % to the cotrimer fraction was achieved.

GC-MS analysis of the liquid product mixture showed that the products obtained were C_{12} compounds formed from two ethene units and one styrene unit, as shown in Scheme 2.8. The by-products of the reaction were 1-hexene from trimerisation of ethene and C_{10} materials from the cotrimerisation of 1-hexene and ethene.



Scheme 2.8 – Overall Cotrimerisation Reaction

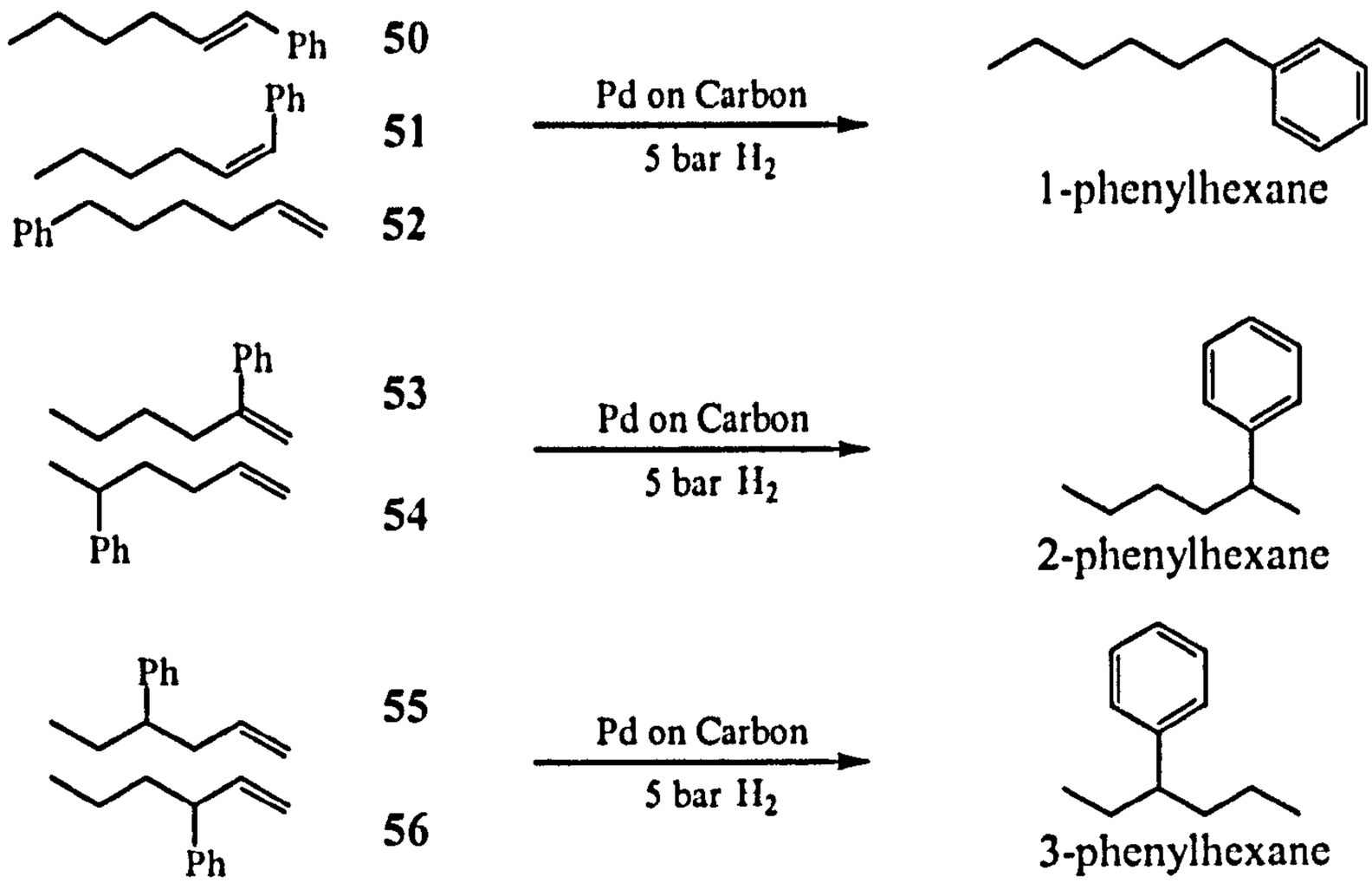
The isomers formed are consistent with the metallocycle mechanism shown in Scheme 2.9. This mechanism is more complicated than simple ethene trimerisation due to the possible of 1,2- or 2,1- regiochemistry of styrene insertion.[4, 22, 82]



Scheme 2.9 - Formation of Isomers in Cotrimerisation of Ethene and Styrene

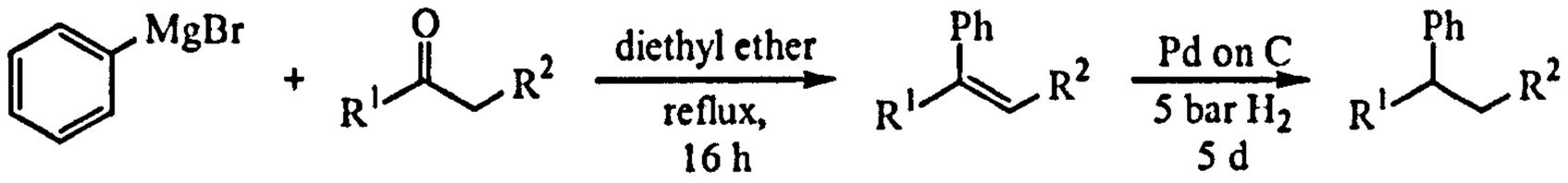
Following catalyst activation, the first step of the catalytic cycle is the coordination of two alkene units, followed by oxidative addition to give metallocyclopentane species (**57** to **59**). Unlike ethene, styrene can insert *via* a 1,2 or 2,1 regiochemistry which leads to the possible formation of three different metallacyclopentanes (**57** to **59**). Metallacyclopentane **57** comes from the insertion of two ethene units, and **58** and **59** are derived from the insertion of one styrene and one ethene unit with **58** having 1,2 and **59** having 2,1 styrene regiochemistry. Metallacycloheptane species **60** to **61** are formed *via* insertion of another ethene or styrene molecule into the metallacyclopentane. This is followed by a β-hydride elimination from either side of the metallacycle, giving seven different chromium hydride species. Finally reductive elimination occurs to give seven possible linear phenylhexene isomers, (*E*)-1-phenyl-1-hexene, **50**, (*Z*)-1-phenyl-1-hexene, **51**, 6-phenyl-1-hexene, **52**, 2-phenyl-1-hexene, **53**, 5-phenyl-1-hexene, **54**, 4-phenyl-1-hexene, **55** and 3-phenyl-1-hexene, **56**. This mechanism is very similar to the mechanism shown for the trimerisation of higher α-olefins in Chapter 1, Scheme 1.24.[82]

The GC data from the catalytic runs showed that only five phenylhexene isomers were present in the resulting cotrimer mixture (see Appendix 8.1 for GC trace). Attempts to fully characterise the cotrimer products was frustrated by the number of isomers with very similar ^{1}H and ^{13}C NMR shifts. Hydrogenation of the cotrimer mixture using palladium on carbon and 5 bar of dihydrogen to the equivalent phenylhexane isomers, simplified identification (Scheme 2.10), where seven possible alkene isomers, from Scheme 2.9, became three possible alkane isomers, 1-phenylhexane, 2-phenylhexane and 3-phenylhexane.[94]



Scheme 2.10 – Hydrogenation of Phenylhexene Cotrimers

Authentic samples of each phenylhexane isomer were synthesised using a literature method, by reacting phenylmagnesium bromide with the corresponding hexanone, in diethyl ether. This was followed by hydrogenation using palladium on carbon under 5 bar of dihydrogen, as shown in Scheme 2.11.[94] 1-Phenylhexane was commercially available. The ^{13}C and ^{1}H NMR spectra and GC data of the cotrimer alkane sample was then compared to that of the authentic samples.



2-Phenylhexane - R^1 = Me, R^2 = *n*Pr
3-Phenylhexane - R^1 = R^2 = Et

Scheme 2.11 – Synthesis of Authentic Phenylhexane Standards

From comparing the cotrimer sample to the authentic samples it was found that the hydrogenated cotrimer mixture contained 1-phenylhexane and 3-phenylhexane; 2-phenylhexane was not present. The percentage of each phenylhexane isomer present was calculated from the GC trace and is reported in Table 2.2.

Table 2.2 – Product Distribution of Hydrogenated Cotrimers

Hydrogenated Cotrimer	Percentage Distribution / %
1-Phenylhexane	84.6 %
2-Phenylhexane	0.0 %
3-Phenylhexane	15.4 %

Within the hydrogenated cotrimer mixture, $[CrCl_3(thf)_3]$/1/MAO system has a selectivity towards 1-phenylhexane of 84.6 % and to 3-phenylhexane of 15.4 %, therefore a selectivity of 84.6 % to isomers **50**, **51** and **52** and a selectivity of 15.6 % to isomers **55** and **56**.

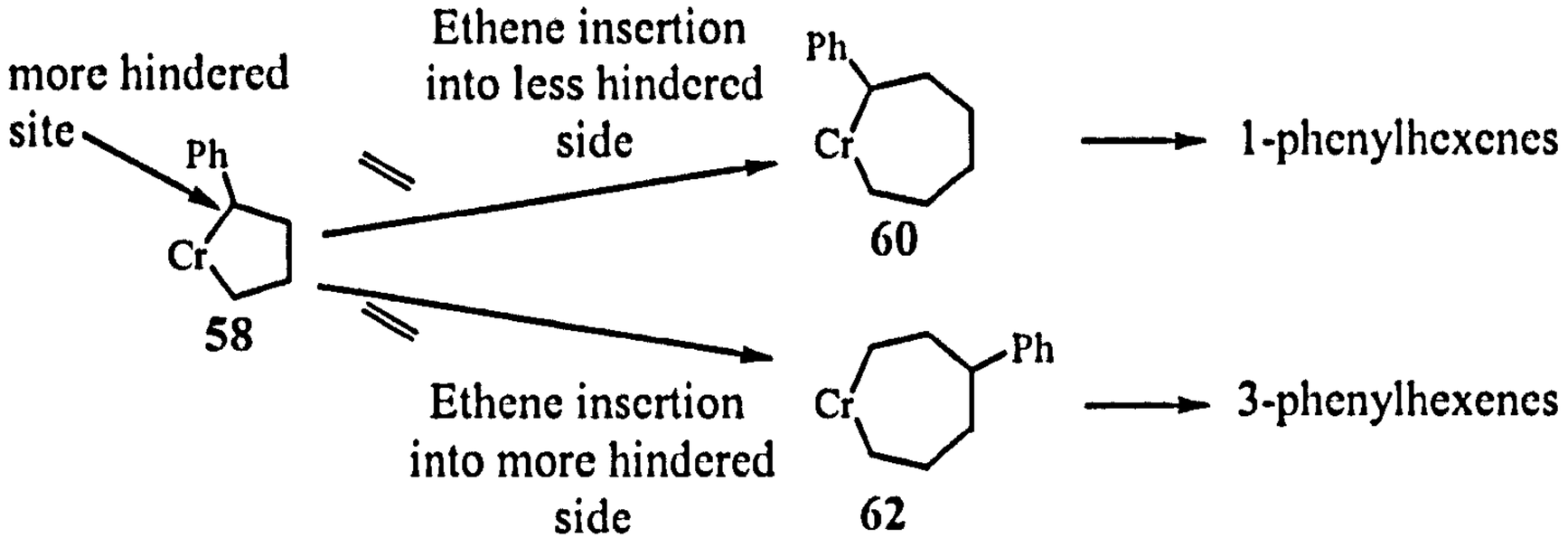
Once the identification of the phenylhexane isomers was achieved, it was possibly to re-examine the ^{13}C NMR spectrum of the original alkene cotrimer mixture and identify the peaks corresponding to each of the 1-phenylhexene isomers, as it was now known that this was the major product. From a comparison with literature ^{13}C NMR shifts, the identification of (*E/Z*)-1-phenyl-1-hexene, **50**, **51** and 6-phenyl-1-hexene, **52** was achieved. Subsequently, using integration of the peaks on the ^{13}C NMR spectrum, the selectivities to each isomer was determined and is shown in Table 2.3.[91, 92] It was not possible to distinguish between isomers **55** and **56** by ^{13}C NMR spectroscopy or by GC, due to very similar shifts and therefore difficult to find the selectivity to each cotrimer. For clarity the 1-phenylhexane and 3-phenylhexane fractions in the hydrogenated cotrimers, will be referred to as the 1-phenylhexene and 3-phenylhexene fractions respectively for the cotrimer mixture.

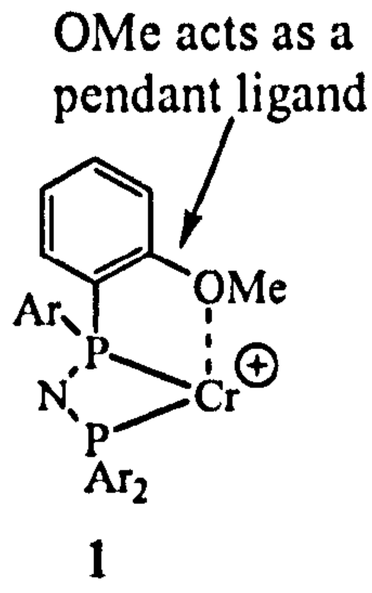
Table 2.3 – Product Distribution within 1-Phenylhexene Fraction

Cotrimer	Selectivity
E-1-phenyl-1-hexene, **50**	54 %
Z-1-phenyl-1-hexene, **51**	13 %
6-Phenyl-1-hexene, **52**	33 %

This system has a selectivity of 54 % towards (*E*)-1-phenyl-1-hexene, **50**, within the 1-phenylhexene fraction and 13 % and 33 % to *Z*-1-phenyl-1-hexene, **51** and 6-phenyl-1-hexene, **52** respectively. The initial aim of the project was to synthesise terminal alkenes for use as comonomers in copolymerisation, therefore this system has an overall selectivity of 27.9 % towards 6-phenyl-1-hexene, **52**.

The resulting selectivity of the $[CrCl_3(thf)_3]$/**1**/MAO system can be explained by referring to the mechanism by which the cotrimer isomers are formed. Firstly, referring to Scheme 2.9, isomer **53** and **54** are formed *via* metallacycloheptane **61**, indicating that this, formed *via* the 1,2 insertion of styrene, is not a significant intermediate. This suggests that the 2,1 insertion of styrene in the mechanism is favoured over 1,2 insertion, which may be due to an interaction between the π system on the phenyl ring of styrene and the chromium centre. Also the carbon atom in the 2 position is more electropositive compared to the carbon atom in the 1 position, due to the electron withdrawing nature of the phenyl ring, so it is more favourable for the metal to bind to this position. All the observed products, **50** - **52** and **55** and **56** can be derived from one metallacyclopentane, **51**, and the major products (**50** - **52**) are obtained from the insertion of ethene into the less hindered side of the metallacyclopentane to give intermediate **60**. It is proposed that the OMe group on the phenyl rings in **1** act as a pendant ligand, increasing the bulk on the metal and therefore the less hindered route is favoured, as shown in Scheme 2.12. Such a pendant donor interaction has been confirmed by Bercaw and co-workers.[5] A purely steric component to this interaction cannot be ruled out in line with observation by Sasol Technology for ethene trimerisation. However the change in selectivity observed with an *ortho* ethyl substituted ligands (*vide infra*) suggests that purely steric interactions are not sufficient to account for this selectivity.





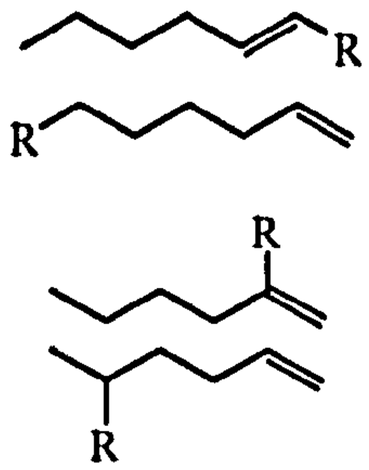
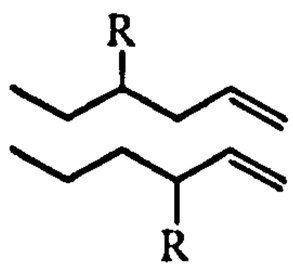
Scheme 2.12 – Formation of Cotrimer Isomers

The selectivity towards internal isomers **50** and **51** is consistent with β-hydride elimination from the more hindered side of intermediate **60**. It is noteworthy that a full statistical distribution of alkene trimers, as would be expected *via* an insertion/elimination mechanism, is not obtained and the aqueous acid used in workup of reaction mixtures does not lead to alkene isomerisation.

2.4.1.2. Comparison of Products to Cotrimerisation of 1-Hexene and Ethene

The by-products of ethene trimerisation using the $[CrCl_3(thf)_3]$/**1**/MAO system are mainly methylnonenes, arising from two ethene units and one 1-hexene unit, this is effectively the cotrimerisation of 1-hexene and ethene.[4] A comparison between the isomers formed in the cotrimerisation of 1-hexene and ethene and the isomers from the cotrimerisation of styrene and ethene is shown in Table 2.4.

Table 2.4 – Product Distribution Comparison for Cotrimerisation of Styrene with Cotrimerisation of 1-Hexene and Ethene

	Styrene (R=Ph)	1-Hexene (R=Bu)
	84.6 %	0 %
	15.4 %	< 5 %

The cotrimerisation of 1-hexene and ethene gives predominantly 2-methylnonene or 2-methylenenonane, from the 1,2 insertion of 1-hexene into the metallocycle mechanism. The cotrimerisation of styrene and ethene gives predominantly 1-phenylhexene isomers, from the 2,1 insertion of styrene into the metallocycle mechanism. The preference of styrene for 2,1 regiochemistry of insertion compared to the 1,2 regiochemistry of 1-hexene has been previously observed.[95-97] It is proposed to be due to electronic contributions of 1-hexene compared to styrene.

2.4.1.3. Effect of Changing Reaction Conditions on Products and Productivity

The aim of this section is to investigate how the productivity and selectivity of the products from the cotrimerisation of ethene and styrene is affected by changing the conditions of the reaction. For a comparison, under the same general conditions as cotrimerisation, it was shown that for ethene trimerisation the $[CrCl_3(thf)_3]$/1/MAO system gave a productivity of 8654 g (g Cr h)$^{-1}$ and a 1-C_6 selectivity (within C_6 fraction) of 86.1 %. Unless otherwise stated, the standard conditions used for the reactions in Table 2.5 are 0.02 mmol of $[CrCl_3(thf)_3]$, 0.02 mmol of **1**, 300 equivalents of MAO, toluene as the solvent, a temperature of 25 °C, 1 bar of ethene and a 1 h run time. The styrene concentration in the reaction vessel was varied from 0 to 6 mol dm^{-3}.

This is shown in runs 2.17 to 2.31 in Table 2.5. The pressure of ethene and total volume was kept constant. The product distribution was calculated from the GC data and the selectivity to 1-hexene is given within the hexene fraction.

Table 2.5 – Cotrimerisation of Styrene and Ethene using $[CrCl_3(thf)_3]$/1/MAO System

Run	Styrene / mol dm^{-3}	Overall TOF / h^{-1}	Productivity / g (g Cr h)$^{-1}$			Selectivity (wt %)				
			Overall	Cotrimer	C_6	Co-trimers	C_6	1-C_6	C_{10}	C_{14}
2.17	0.04	4430	7570	802	6768	10.6	67.2	94.0	21.4	0.8
2.18	0.1	3954	6774	718	6056	6.9	71.6	98.9	13.7	0.2
2.19	0.4	4660	9490	4052	5438	42.7	38.4	98.9	18.1	0.8
2.20	1.0	3630	8472	5940	2532	64.8	21.5	96.6	13.8	0.0
2.21	1.6	3245	8264	6339	1925	76.7	10.5	97.8	5.3	0.0
2.22	6.0	2674	7926	7593	333	95.8	4.2	-[h]	0.0	0.0
2.23[a]	0.1	2787	4844	722	4122	14.9	53.4	99.2	27.9	3.8
2.24[a]	0.4	855	1669	607	1062	36.4	53.5	96.3	10.1	0.0
2.25[a]	1.0	2295	3305	2489	816	75.3	22.1	93.1	2.6	0.0
2.26[a]	1.6	1106	2801	2134	667	76.2	22.7	81.6	1.1	0.0
2.27[b]	6.0	1120	3306	3150	156	95.3	3.9	-[h]	0.7	0.0
2.28[c]	6.0	1720	4579	3787	792	82.7	16.0	89.1	1.3	0.0
2.29[d]	6.0	1966	5321	4518	803	84.9	15.9	99.8	0.0	0.0
2.30[e]	ethene only	5357	-	-	8654	-	73.0	86.1	25.0	2.0
2.31[f]	6.0	0	0	0	-	0	-	-	-	-
2.32[g]	6.0	0	0	0	0	0	0	-	0	0

[a] 2 h run time, [b] 6 h run, [c] 70 °C, [d] cyclohexane used as solvent, [e] ethene trimerisation, [f] styrene homotrimerisation run with no ethene, [g] blank run with styrene and ethene but no ligand, [h] not detectable.

Two control runs were performed, run 2.31 and 2.32 in Table 2.5, these showed that no cotrimerisation occurs in the absence of ligand (run 2.32) or in the absence of ethene (run 2.31), styrene homotrimerisation, does not occur. For ethene trimerisation the productivity or turnover frequency (TOF) of the system can be calculated from the mass

gain of the reaction vessel, as the only monomer is ethene.[2] Due to the difference in molecular weights of the products (hexene and the cotrimers) and that hexene consumes three ethene molecules, whereas phenylhexene consumes two ethene molecules, the productivity and TOF could not be directly calculated from the mass gain of the reaction vessel. Once cotrimers were identified, the cotrimer productivity and TOF could be found. Cotrimer productivity and TOF were calculated from the mass of cotrimers produced, which was in turn calculated from the mass gain, as follows:

Ratio of cotrimer to hexene

$$R = \frac{\%(\text{cotrimer})}{100 - \%(\text{cotrimer})}$$

Fraction of ethene comsumed in cotrimer compared to styrene

$$\text{Frac(cotrimer)} = \frac{\text{Mw (ethene)}}{\text{Mw(ethene)} + \text{Mw(styrene)}} = 0.35$$

Mass cotrimer produced

$$\text{m(cotrimer)} / \text{g} = \frac{\text{mass gain of run} \times \text{Frac(cotrimer)}}{1 + \text{Frac(cotrimer)} \times R}$$

Productivity of cotrimer only

$$\text{Prod(cotrimer)} / \text{g(g Cr h)}^{-1} = \frac{\text{m(cotrimer)}}{\text{Mw(Cr)} \times \text{moles(Cr)} \times \text{run time}}$$

$$\text{m(1-hexene)} / \text{g} = \frac{\text{mass gain of run}}{1 + \text{Frac(cotrimer)} \times R}$$

$$\text{TOF (overall)} / \text{h}^{-1} = \frac{\text{m(1-hexene)}}{\text{Mw(hexene)} \times \text{run time} \times \text{Mw(Cr)}}$$

It can be seen from Table 2.5 that as the concentration is increased the TOF decreases, showing a decrease in activity. Adding styrene to the reaction vessel slows down the rate of cotrimerisation, where at a concentration of 6.0 mol dm^{-3} of styrene, a TOF of 2674 h^{-1} is obtained (run 2.22). One reason for a decrease in activity may be due to catalyst poisons in styrene, which were not removed in the purification process.

As expected, as the concentration of styrene is increased the activity towards cotrimerisation increases and the ethene trimerisation activity decreases, see Runs 2.17 to 2.22 in Table 2.5. Below a concentration of 1.0 mol dm^{-3}, an increase in the concentration produces a larger change in the productivity than above 1.0 mol dm^{-3}. As

each reaction proceeds, styrene is being consumed and therefore the concentration is decreasing. This may have an effect on the productivity of a run using low styrene concentrations but will have little effect on, for example, run 2.22 using 6 mol dm^{-3} of styrene as an excess of styrene is also seen in the GC trace.

At 6.0 mol dm^{-3} (run 2.22 in Table 2.5), a selectivity to the cotrimer fraction of 95.8 % is achieved, this selectivity is not affected by run time, as the selectivities towards hexene and cotrimers are very similar over 1 h (runs 2.16) and 2 h runs. After 6 h (run 2.27 in Table 2.5) the selectivity to cotrimers has decreased to 82.7 % and the TOF decreases to 1120 h^{-1}, indicating catalyst deactivation over time. The cotrimer selectivity increases rapidly as the concentration of styrene is increased. At 1 mol dm^{-3} the percentage of cotrimers is over 60 %, reaching 95.8 % at 6.0 mol dm^{-3} of styrene.

Generally catalytic runs were carried out at 25 °C, although a small (<10 °C) amount of exotherm was observed during the reaction. Run 2.28 in Table 2.5 was run at 70 °C, with a styrene concentration of 6 mol dm^{-3}. The TOF and cotrimer selectivity for this run was 1,720 h^{-1} and 82.7 % respectively, compared to 2,674 h^{-1} and 95.8 % for run 2.22 at 25 °C. At this temperature the drop in activity may be due to catalyst decomposition to non-active species. A similar observation was made by Wass and co-workers, who found that when this system is used for ethene trimerisation, using 2 bar of ethene, at 80 °C, the TOF was 2,976 h^{-1} compared to 6,131 h^{-1} for 1 bar of ethene at 25 °C.[4]

As previously stated in Section 2.4.1.1 there are 8 possible cotrimer products, although only 5 products are formed. Table 2.6 and Figure 2.4 show how the ratio of each cotrimer changes with styrene concentration, shown as a percentage.

Table 2.6 – Change in Ratio of Cotrimers with Concentration

Run	Styrene Concentration / mol dm^{-3}	Total Cotrimer Selectivity / %	Cotrimers Product Distribution (wt %)						
			50	51	52	53-54	55-56	In 55-56 Fraction[a]	
								A	B
2.17	0.04	10.6	49.2	13.3	20.9	0.0	16.6	9.1	7.5
2.18	0.1	6.9	53.1	9.6	21.1	0.0	16.2	8.5	7.7
2.19	0.4	42.7	53.3	9.9	20.6	0.0	16.2	8.5	7.7
2.20	1.0	64.8	51.1	9.6	20.7	0.0	18.6	9.3	9.3
2.21	1.6	76.7	52.1	12.1	19.1	0.0	16.7	8.6	8.1
2.22	6.0	95.8	54.5	8.6	22.2	0.0	14.7	7.8	6.9
2.23	0.1	14.9	55.9	11.1	18.8	0.0	14.2	7.2	7.0
2.24	0.4	36.4	54.0	9.3	21.5	0.0	15.2	7.7	7.5
2.25	1.0	75.3	56.1	9.0	21.8	0.0	13.2	7.0	6.1
2.26	1.6	76.2	55.1	9.0	22.3	0.0	13.6	7.2	6.4
2.27[b]	6.0	95.3	56.3	8.8	21.5	0.0	13.4	7.2	6.2
2.28[c]	6.0	82.7	47.7	10.7	21.9	0.0	19.8	10.0	9.8
2.29[d]	6.0	84.9	55.6	9.2	20.1	0.0	15.1	9.2	5.9

[a] Calculated as a percentage of whole cotrimer product and not as percentage of 55-56 fraction; [b] 6 h run; [c] run at 70 °C; [d] cyclohexane as solvent.

In Table 2.6 isomers **55** and **56** are referred to as **A** and **B** when calculating the ratio of each; it not possible to accurately assign isomer **55** or **56** to the relevant peaks on the GC trace due to the similarities of the two isomers in ^{13}C NMR spectroscopy.

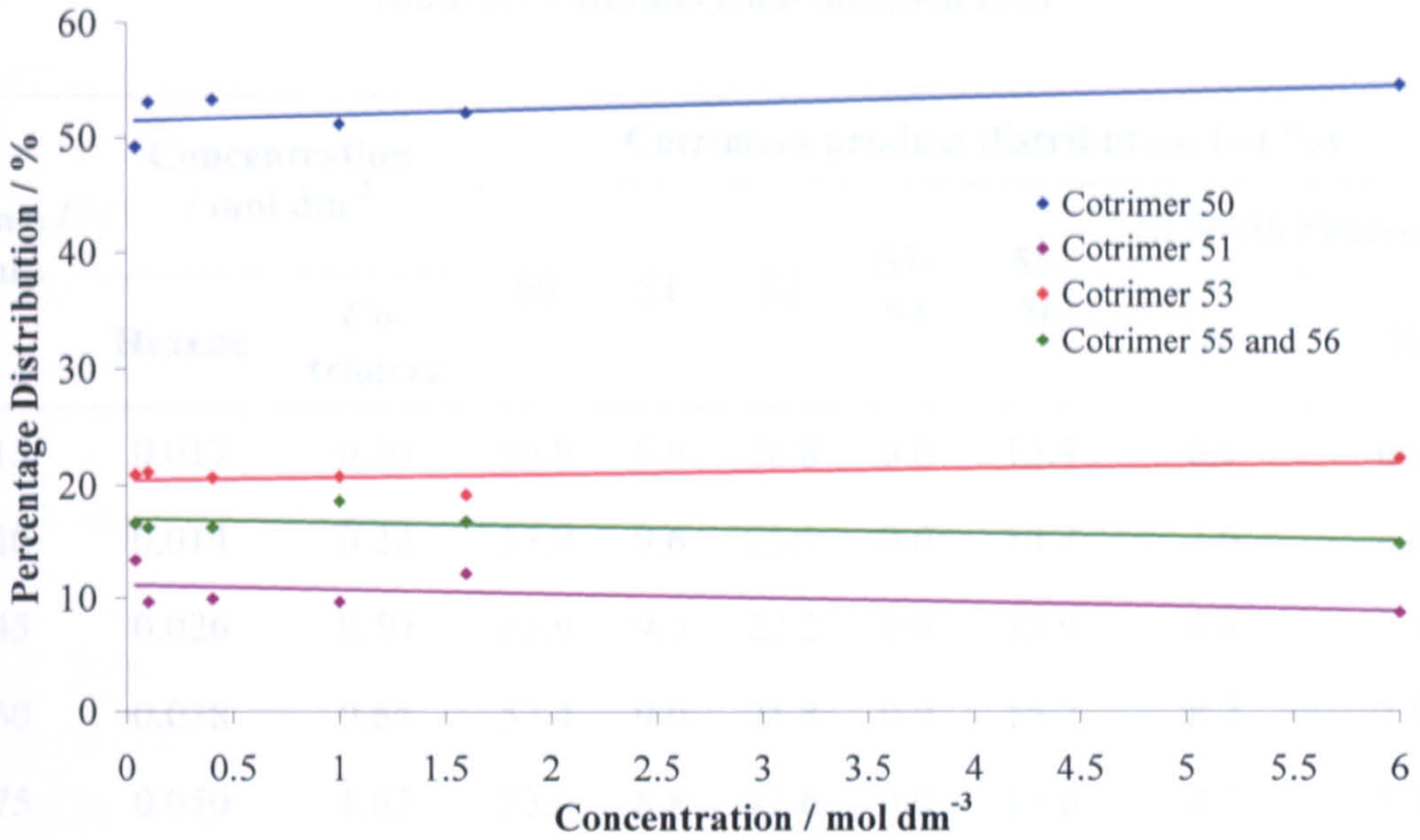


Figure 2.4 – Change in Product Distribution with Concentration for 1 h Run

The ratio of each cotrimer stays constant and is not concentration dependant, this pattern is also true for the set of reactions run for 2 h (run 2.23 - 2.26 in Table 2.6) and 6 h (run 2.27 in Table 2.6). Temperature has an effect on cotrimer distribution (run 2.28 in Table 2.6), with an increase in the formation of isomers **55** and **56**.

Run 2.29 in Table 2.5 shows results obtained from a run using cyclohexane as the solvent instead of toluene. A TOF of 1966 h^{-1} was achieved, which is lower than that obtained for toluene (2674 h^{-1}, run 2.22 in Table 2.5) and the selectivity towards the cotrimer fraction is also lower, at 84.9 %, although the distribution of cotrimer isomers within the cotrimer fraction (Run 2.29, Table 2.5) is not affected by the solvent.

In order to investigate how the percentage of products produced changed throughout the reaction and if the catalyst degrades over time, a run was performed at a styrene concentration of 6 mol dm^{-3} and 25 °C, using 0.02 mmol $[CrCl_3(thf)_3]$, 0.02 mmol **1**, 300 equivalents of MAO cocatalyst, toluene and a total volume 44 mL. Samples were taken every 15 minutes for two hours and mesitylene was used as an internal standard, in order to calculate the concentration of cotrimers and 1-hexene in the solution. The results are shown in Table 2.7 and in Figure 2.5.

Table 2.7 – Results from Sampled Run

Time / min	Concentration / mol dm^{-3}		Cotrimers product distribution (wt %)						
			50	51	52	53-54	55-56	In 55-56 Fraction[a]	
	Hexene	Co-trimers						A	B
15	0.017	0.20	56.9	8.9	20.8	0.0	13.4	6.5	6.9
30	0.014	0.22	53.0	9.6	23.1	0.0	14.2	7.6	6.6
45	0.026	0.50	52.9	9.0	22.2	0.0	15.9	8.4	7.5
60	0.038	0.64	53.4	9.0	21.8	0.0	15.7	8.2	7.5
75	0.050	1.07	53.0	8.8	22.6	0.0	15.6	8.3	7.3
90	0.046	1.07	53.9	9.3	20.5	0.0	16.3	8.3	8.0
105	0.077	1.05	53.8	8.8	22.7	0.0	14.7	8.0	6.7
120	0.082	1.1	53.3	8.8	22.4	0.0	15.4	8.1	7.3
180	0.040	1.15	56.7	8.8	22.4	0.0	12.2	6.3	5.9

[a] Calculated as a percentage of whole cotrimer product and not as percentage of 55-56 fraction, 55 and 56 cannot be distinguished.

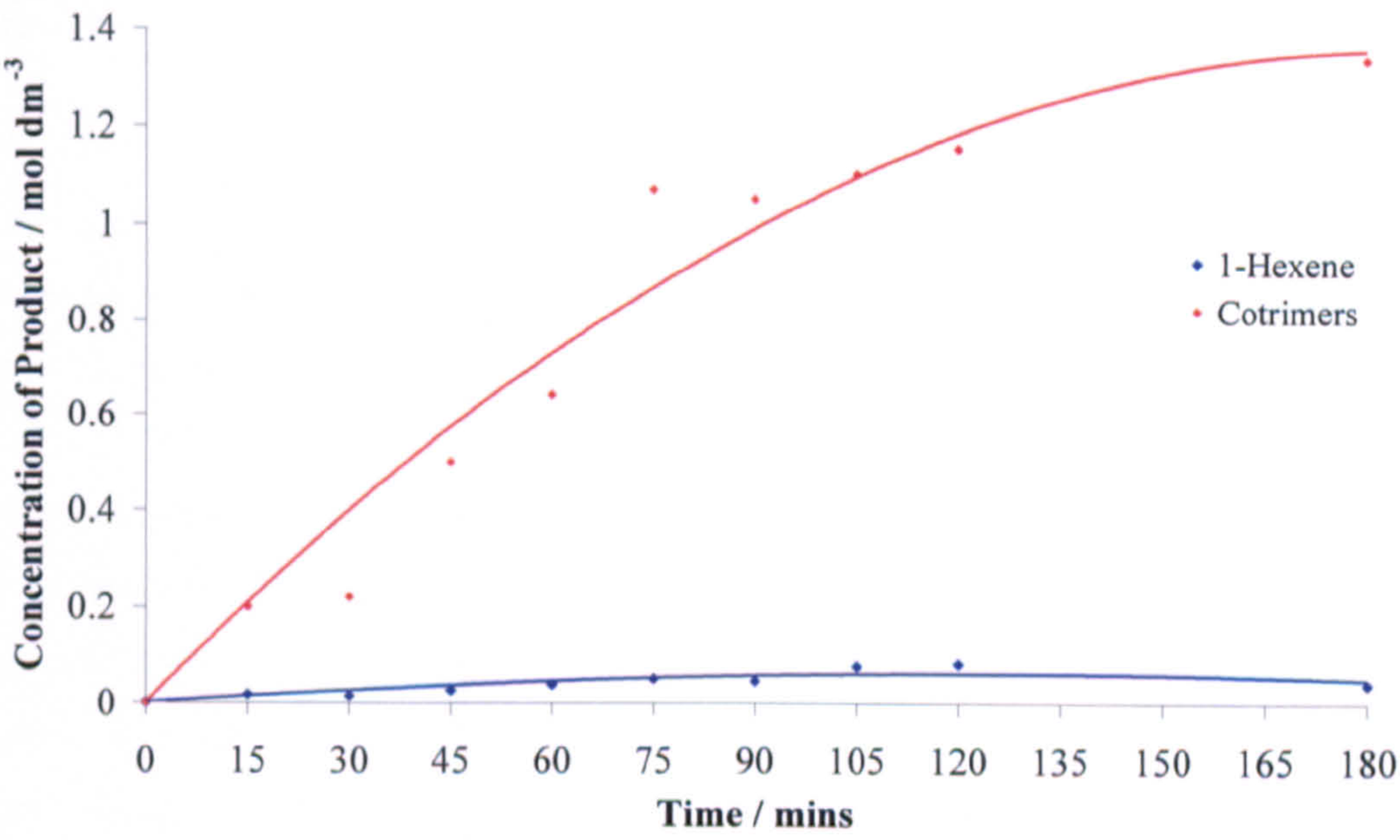


Figure 2.5 – Change in Product Composition over Time

Figure 2.5 shows that, within experimental error, both hexene and the cotrimers are initially formed uniformly over time, but after about 90 min the production slows down, presumably due to a reduction in styrene concentration as the reaction proceeds, although this could also be due to catalyst decomposition. The cotrimer concentration increases rapidly compared to 1-hexene, showing that at high concentrations of styrene, cotrimer formation is favoured over 1-hexene formation.

2.4.1.4. Cotrimerisation of Ethene with Substituted Styrene Comonomer

The investigation was extended to substituted styrene derivatives and the results are shown in Table 2.8. Unless otherwise stated, the standard conditions were 0.02 mmol of $[CrCl_3(thf)_3]$, 0.02 mmol of ligand, 300 equivalents of MAO, 1.2 mol dm^{-3} of substituted styrene comonomer, toluene (total volume of 6 mL) a temperature of 25 °C, 1 bar of ethene and reaction time of 1 hour.

Table 2.8 – Cotrimerisation of Ethene and Substituted Styrene Derivatives

Run	Comonomer	Overall TOF / h^{-1}	Productivity / g (g Cr h)$^{-1}$		Product Distribution (wt %)			
			Overall	Co-trimer	Co-trimers	C_6	1-C_6	C_{10}
2.22	styrene	2674	7926	7593	95.8	4.2	-[b]	0.0
2.33[a]	4-methylstyrene	2529	3724	2872	87.7	12.3	62.4	0.0
2.34	2-chlorostyrene	143	231	0	0.0	100.0	77.7	0.0
2.35	4-chlorostyrene	713	1885	1363	72.3	19.1	86.8	8.6
2.36	3-nitrostyrene	232	375	0	0.0	67.9	83.6	32.1
2.37	4-methoxystyrene	134	268	94	35.0	59.8	81.0	5.2
2.38	2,4,6-trimethyl-styrene	411	663	0	0.0	82.6	77.5	17.4
2.39	4-vinylpyridine	0	-	-	0.0	100.0	-	0.0
2.40	2-vinylpyridine	0	-	-	0.0	100.0	-	0.0
2.41	vinylcyclohexane	0	-	-	0.0	100.0	[c]	0.0

[a] 5.2 mol dm^{-3} 4-methylstyrene, total volume 44 mL, [b] percentage too low to calculate 1- C_6 selectivity, [c] Could not be determined as coincided with comonomer peak;

The productivity observed for all substituted derivatives is lower than that for styrene. The selectivity towards cotrimer products, for 4-methylstyrene, is similar to styrene. 4-chlorostyrene has a lower selectivity than styrene for these products. A significantly lower productivity and selectivity is observed with 4-methoxystyrene (run 2.27 in Table 2.8). This observation may be due to electronic effects of the methoxy group but as 4-methoxystyrene gives similar electronic properties to 4-methylstyrene, it is more likely to be due to poisoning of the electrophilic catalyst centre by binding to the OMe group. It can be seen from Table 2.8 that the styrene derivatives with *para* substituents produced co-trimers, whereas the *ortho* or *meta* substituted derivatives did not. For example using 2-chlorostyrene (run 2.34 in Table 2.8) does not produce cotrimers, whereas using 4-chlorostyrene (run 2.28 in Table 2.8) does produce cotrimers, with a cotrimer productivity of 1363 g (g Cr h)$^{-1}$ and a selectivity to cotrimers of 72.3 %. This may be because the derivatives with *ortho* substituents are too bulky to be incorporated

into the growing metallocycle, whereas the *para* substituted derivatives have less steric bulk in the region adjacent to the vinyl group.

Referring to Scheme 2.9, it can be seen that the route that forms cotrimer isomers **50 - 52**, **55** and **56** involves the formation of chromacyclopentane **57** and chromacycloheptanes **60** or **62** from the 2,1 insertion of styrene (Figure 2.6). In both intermediates the aryl group is positioned so that the delocalised π-system may interact with the metal centre. Intermediates **58**, **60** or **62** with aryl groups with *ortho* substituents are much more hindered than when the R group is in the *para* position.

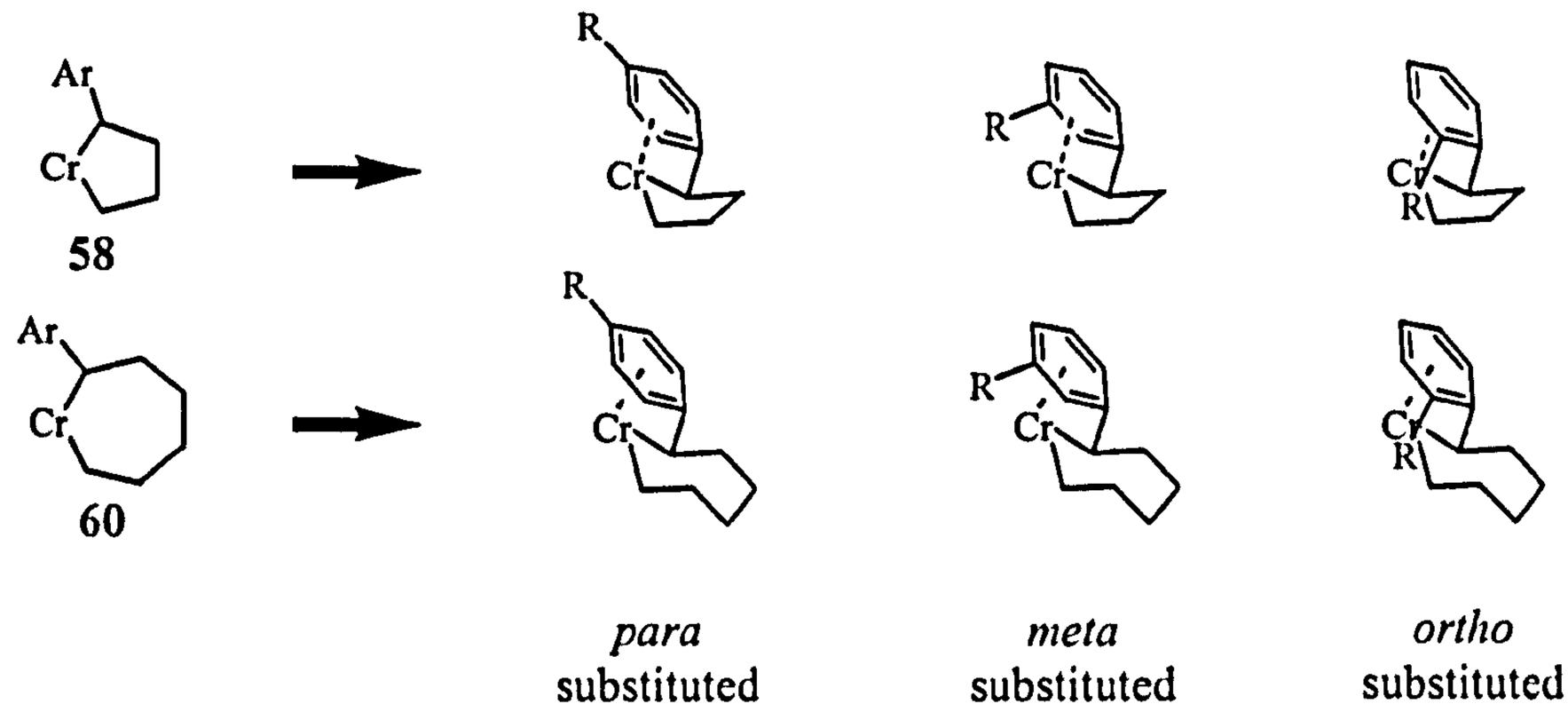


Figure 2.6 – Effect of Position of R for Substituted Styrene Derivatives

The ring-saturated version of styrene, vinyl cyclohexane, run 2.41, produced no cotrimers. This is surprising but suggests that having the phenyl ring is important and supports the theory that the phenyl ring interacts with the metal centre. 2-Vinylpyridine and 4-vinylpyridine are sterically equivalent to styrene and, like styrene, contain a delocalised π-system, but do not form cotrimers. It seems likely that the nitrogen binds irreversibly to the metal centre and shuts down catalysis.

Table 2.9 shows the product distribution of the different cotrimers for each of the successful styrene derivatives. **50** to **56** in Table 2.9 refer to the styrene/ethene cotrimer analogues, where here the substituted versions of these isomers are formers.

Table 2.9 – Cotrimer Distribution of Cotrimerisation of Ethene with Substituted Styrene Derivatives

Run	Comonomer	Cotrimers Product Distribution (wt %)						
		50	51	52	53-54	55-56	In 55-56 Fraction[a]	
							A	B
2.22	styrene	54.5	8.6	22.2	0.0	14.7	7.8	6.9
2.33	4-methylstyrene	44.4	7.4	25.9	0.0	22.2	12.0	10.2
2.35	4-chlorostyrene	74.2	8.1	12.6	0.0	5.1	2.1	2.0
2.36	4-methoxystyrene	48.7	9.5	25.0	0.0	16.8	8.8	8.0

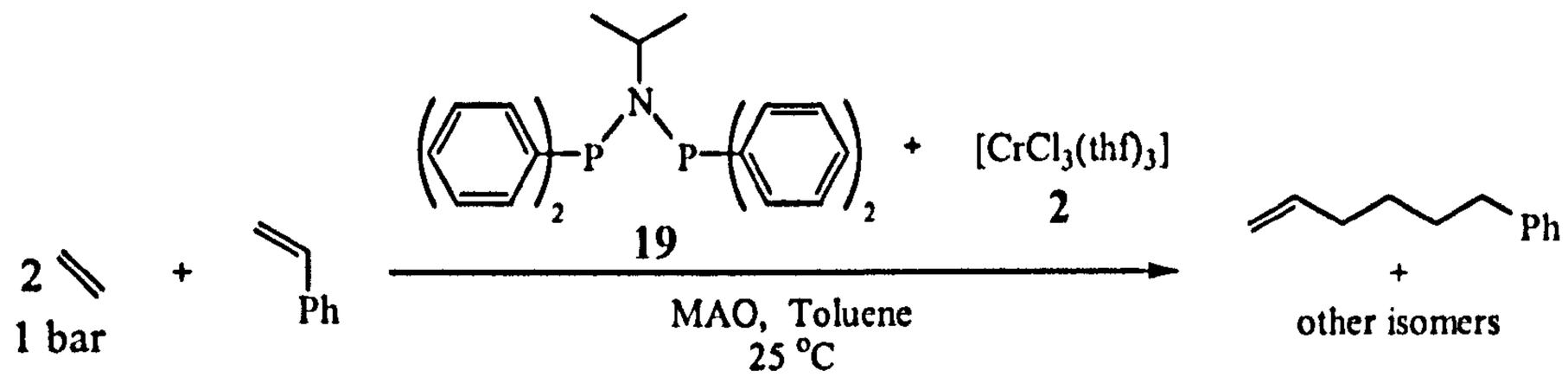
[a] 5.2 mol dm^{-3} 4-methylstyrene, total volume 44 mL.

4-Methylstyrene and 4-methoxystyrene show a similar distribution to styrene. 4-chlorostyrene has a higher percentage of the internal isomer, substituted version of isomer **50**. It is unclear as to why this change in product distribution occurs, although referring to the mechanism in Scheme 2.9, the formation of the isomer **50** analogue is from intermediate **60**, with β-hydride elimination of **60** on the side of the phenyl group. This suggests that the larger chlorine substituent forces β-hydride elimination in this position, also the electron donating properties of the chlorine into the phenyl group may weaken the chromium-phenyl interaction.

2.4.2. $[CrCl_3(thf)_3]$/*N,N*-bis(diphenylphosphino)isopropylamine, 19/MAO System

At 45 bar of ethene and 45 °C, the $[CrCl_3(thf)_3]$/19/MAO system, reported by Bollmann and co-workers was found to tetramerise ethene to 1-octene, with a selectivity to C_8 of 68.3 %, of which 98.9 % is 1-octene and a productivity of 272,400 g (g Cr h)$^{-1}$.[47] This system was chosen for the co-oligomerisation of styrene and ethene at an ethene

pressure of 1 bar and 25°C; the same general conditions were used as that for the $[CrCl_3(thf)_3]$/1/MAO system, as shown in Scheme 2.13.



Scheme 2.13 – $[CrCl_3(thf)_3]$/19/MAO System

As with the $[CrCl_3(thf)_3]$/1/MAO system, GC analysis of the liquid product mixture showed that the products obtained were phenylhexene isomers, in contrast to the selectivity for tetramerisation products observed in ethene homo-oligomerisation seen for this catalyst.[47] The percentage selectivity to cotrimers is 100 %; no hexene was produced. Table 2.10 shows the results obtained from this system, using 0.02 mmol of $[CrCl_3(thf)_3]$, 0.02 mmol **19**, 1 bar of ethene and 6.0 mol dm^{-3} of styrene, at 25 °C for 1 h.

Table 2.10 – Styrene/Ethene Cotrimerisation Using $[CrCl_3(thf)_3]$/19/MAO System

Run	Overall TOF / h^{-1}	Productivity / g (g Cr h)$^{-1}$			Product Distribution (wt %)				
		Overall	Cotrimer	1-Hexene	Co-trimers	C_6	1-C_6	C_{10}	C_{14}
2.42	1232	3791	3791	0	100.0	0.0	0.0	0.0	0.0
2.43[a]	821	2527	2527	0	94.5[c]	0.0	0.0	0.0	0.0
2.44[b]	786	2418	2418	0	100.0	0.0	0.0	0.0	0.0

[a] 70 °C, [b] cyclohexane used as solvent, [c] 5.5 % unidentified oligomers.

Run 2.42 shows that, in comparison, the TOF and overall productivity are half that of the $[CrCl_3(thf)_3]$/1/MAO system. Increasing the temperature to 70 °C (run 2.43) or using cyclohexane as the solvent (run 2.44) seems to decrease the productivity. A small amount of unidentified higher oligomer products were observed with **19** as the ligand at

70 °C (run 2.43 in Table 2.10). It seems that at elevated temperatures that more than one styrene unit, or greater than three monomer units may be incorporated into the products, albeit with low selectivity.

Table 2.11 – Product Distribution of [$CrCl_3(thf)_3$]/19/MAO System for Cotrimerisation

Run	Cotrimers Product Distribution (wt %)						
	50	51	52	53-54	55-56	In 55-56 Fraction[c]	
						A	B
2.42	4.1	0.3	0.4	0.0	95.2	50.4	44.8
2.43[a]	6.7	0.9	0.5	0.0	91.9	49.5	42.4
2.44[b]	11.4	0.7	0.6	0.0	87.3	46.4	40.9

[a] 70 °C, [b] cyclohexane used as solvent, [c] overall selectivity.

The product distribution, under standard conditions (run 2.42, Table 2.11) is 4.8 % (*E/Z*)-1-phenyl-1-hexene, **50**, **51** and 6-phenyl-1-hexene, **52** and 95.2 % 4-phenyl-1-hexene, **55** and 3-phenyl-1-hexene, **56**. There was no 2-phenyl-1-hexene, **53** or 5-phenyl-1-hexene, **54** present. Although the products are still consistent with a route involving the 2,1 insertion of styrene, the selectivity of this system is different to that of [$CrCl_3(thf)_3$]/1/MAO system, favouring the formation of more branched isomers over linear. The origin of this selectivity control is not clear leading to the investigation of a wider range of ligands in Section 2.4.3. Increasing the reaction temperature to 70 °C (run 2.43 in Table 2.11), decreased the selectivity to isomers **55** and **56** to 91.9 %.

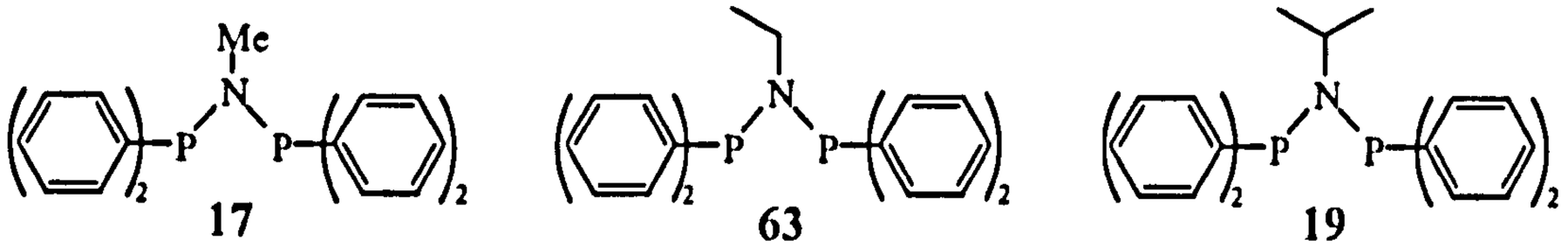
2.4.3. Ligand Effects

2.4.3.1. *N,N*-bis(diarylphosphino)alkylamine Ligands for Cotrimerisation of Ethene and Styrene

A variety of PNP ligand were synthesised and tested for ethene and styrene cotrimerisation. The PNP ligands were synthesised using a variety of methods adapted from literature methods.[36, 37, 41, 42, 98] These syntheses are discussed further in Chapter 5.

Unless otherwise stated the conditions used for catalysis were 0.02 mmol of $[CrCl_3(thf)_3]$, 0.02 mmol of PNP ligand, 300 equivalents of MAO cocatalyst, a temperature of 25 °C, 1 bar of ethene, and a reaction time of 1 hour. The results obtained are shown in Tables 2.12 to 2.16, the productivity in each table was determined from the mass gain of the reaction vessel and the cotrimer selectivity was determined from the GC data. For a comparison each table contains run 2.22 (originally from Table 2.5 in Section 2.4.1.3) showing the results from the $[CrCl_3(thf)_3]$/1/MAO system.

Figure 2.7 shows a series of PNP ligands with alkyl substituents on the nitrogen backbone. The $[CrCl_3(thf)_3]$/19/MAO system, which was found to be highly active for ethene tetramerisation (see Section 1.3.1), was shown in Section 2.4.2 to form mainly **55** and **56**, leading to investigation into other PNP ligands.[55] The productivities and selectivities obtained from systems using these PNP ligands are shown in Table 2.13.



17 **63** **19**

Figure 2.7 – PNP Ligands with Alkyl Substituents on the Nitrogen

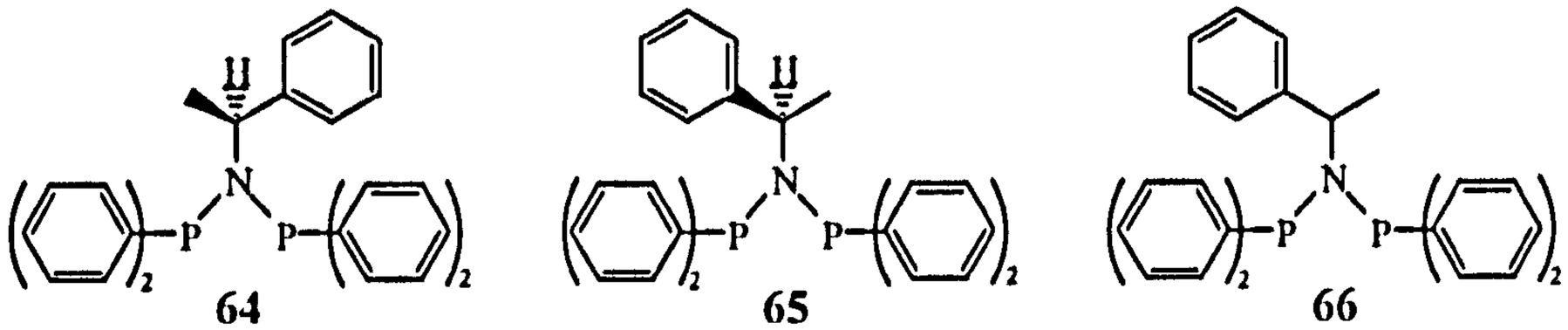
Table 2.12 – Cotrimerisation with the PNP Ligands in Figure 2.7

Run	Ligand	Productivity / g (g Cr h)$^{-1}$	TOF of Cotrimer / h^{-1}	Cotrimers Product Distribution (wt %)						
				50	51	52	53-54	55-56	In 55-56 Fraction[a]	
									A	B
2.22	1	7926	2674	54.5	8.6	22.2	-	14.7	7.8	6.9
2.45	17	6044	1961	24.4	10.3	7.2	-	58.1	28.0	27.8
2.46	63	8049	2621	14.0	3.9	3.3	-	78.9	39.3	39.6
2.42[c]	19	3791	1232	——	4.8	——	-	95.2	47.0	48.2

[a] overall selectivity; [b] Percentage too small to distinguish cotrimers; [c] see Table 2.10

PNP ligands with alkyl substituents on the nitrogen (Figure 2.7) were highly active for cotrimerisation, although generally less active than ligand **1**, (Table 2.12). There is no obvious correlation between the size of the alkyl group and the activity, as in run 2.46 ligand **63** gave a cotrimer TOF of 2621 h^{-1}. The selectivity is affected by the size of the alkyl group, the selectivity towards isomers **55** and **56** is 58.1 % for **17** (run 2.45 in Table 2.12), increasing to over 95 % for the bulkier ligand **19** (run 2.42 in Table 2.12). Therefore the larger the group on the nitrogen, the higher the selectivity is towards isomers **55** and **56**. The optimum size for the group on the nitrogen, with respect to TOF, is an ethyl group, although it is not clear as to why this is the case. It is noteworthy that the profound effect of this group in ethene homotri/tetramerisation is not understood.

Figure 2.8 shows PNP ligands with α-methylbenzyl groups on the nitrogen.



64 S Isomer

65 R Isomer

66 R/S Isomer

Figure 2.8 – Isomers of N,N-bis(diphenylphosphino)-α-methylbenzylamine

Table 2.13 – Cotrimerisation with PNP Ligands in Figure 2.8

Run	Ligand	Productivity / g (g Cr h)$^{-1}$	TOF of Cotrimer / h^{-1}	Cotrimers Product Distribution (wt %)						
				50	51	52	53-54	55-56	In 55-56 Fraction[a]	
									A	B
2.22	1	7926	2674	54.5	8.6	22.2	-	14.7	7.8	6.9
2.47	64	2692	878	——	4.9[b]	——	-	95.1	53.2	41.9
2.48	65	3022	983	——	5.9[b]	——	-	94.1	59.6	34.5
2.49	66	3132	1018	1.1	3.9	5.4	-	90.0	49.8	40.2

[a] Calculated as a percentage of whole cotrimer product and not as percentage of 55-56 fraction, [b] Percentage too small to distinguish cotrimers.

Table 2.13 shows the results obtained for the PNP ligands **64** to **66** shown in Figure 2.8. Increasing the size of the group on the nitrogen to a α-methylbenzyl group decreases the TOF to 878 – 1012 h^{-1}, the selectivity to isomers **55** and **56** was over 90% for each PNP in Table 2.13. Cotrimer isomers **55** and **56** have a chiral centre and so enantomerically pure PNP ligands **64** and **65** were tested. Chiral GC showed that there was no control over chirality, with little change in the product distribution between the R/S isomer, **64**, and the S isomer, **65** or the R isomer, **66**.

Figure 2.9 shows a series of PNP ligands in which the alkyl substituents on the aryl groups has been modified, with the results obtained for these ligands in Table 2.14.

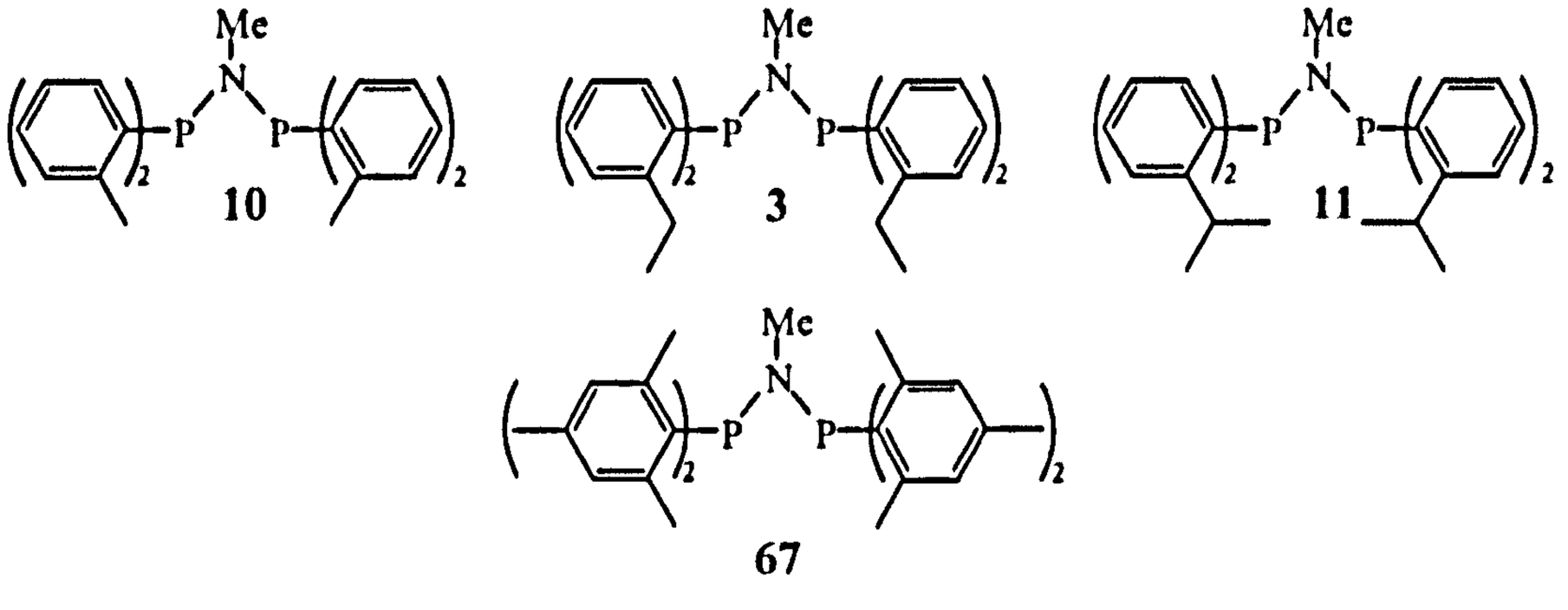


Figure 2.9 – PNP Ligand with Alkyl Substituents on Aryl Groups

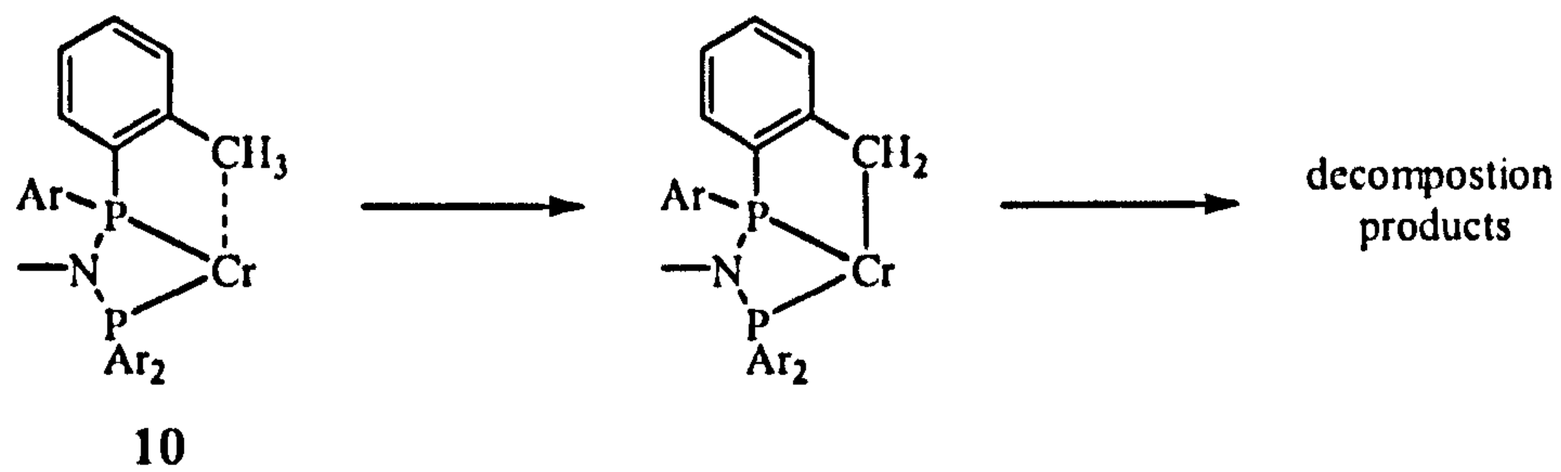
Table 2.14 – Cotrimerisation with PNP Ligands in Figure 2.9

Run	Ligand	Productivity / g (g Cr h)$^{-1}$	TOF of Cotrimer / h^{-1}	Cotrimers Product Distribution (wt %)						
				50	51	52	53-54	55-56	In 55-56 Fraction[a]	
									A	B
2.22	1	7926	2674	54.5	8.6	22.2	-	14.7	7.8	6.9
2.45	17	6044	1961	24.4	10.3	7.2	-	58.1	28.0	27.8
2.50	10	30	10	14.2	9.0	15.4	-	61.4	34.2	27.2
2.51	10[b]	0	0	-	-	-	-	-	-	-
2.52	3	0	0	-	-	-	-	-	-	-
2.53	11	24	3	-	-	-	-	100.0	53.5	46.5
2.54	67	0	0	-	-	-	-	-	-	-

[a] Calculated as a percentage of whole cotrimer products and not as percentage of 57-58 fraction; [b] 70 °C.

Compared to **1** and **17** (with a phenyl groups), the productivity from these ligands is greatly reduced, with a TOF of only 10 h^{-1} for **10** (run 2.50 in Table 2.14). In run 2.52, ligand **3** is sterically similar to **1** although unlike **1**, is not active for cotrimerisation, showing the reason for the high activity of **1** is not due to the steric bulk of the ligand. Cotrimerisation does not seem to occur with systems with alkyl substituents in the *ortho* position. As expected, the trimethyl derivative, **67**, also showed no activity. A possible

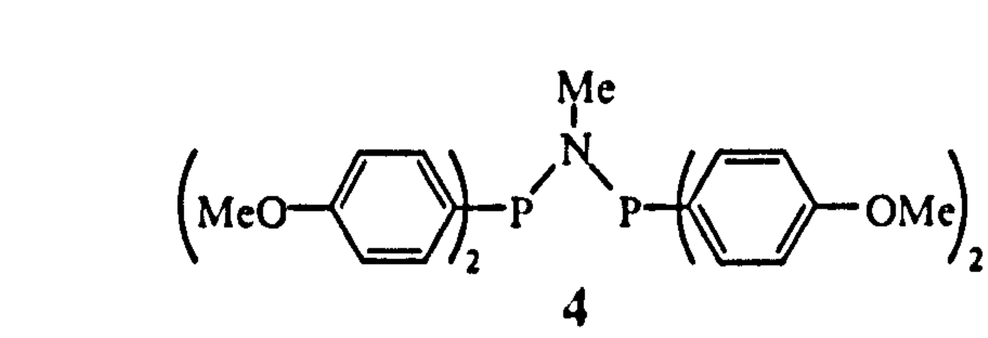
reason for this low productivity may be because the alkyl groups in the *ortho* position of each phenyl ring can undergo cyclometallation stopping catalysts from proceeding or leading to decomposition, as shown in Figure 2.10.



10

Figure 2.10 – Cyclometallation of Ligand 10 to Chromium Centre

Due to the unique selectivity of 1 over other PNP ligands tested, a set of ligands were tested with oxygen donating substituents related to the OMe group in 1. The ligands tested are shown in Figure 2.11 and the results obtained are given in Table 2.15. The synthesis of 68 and 69 is discussed in Chapter 5.



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68

69

Figure 2.11 - PNP Ligands with Oxygen Based Substituents

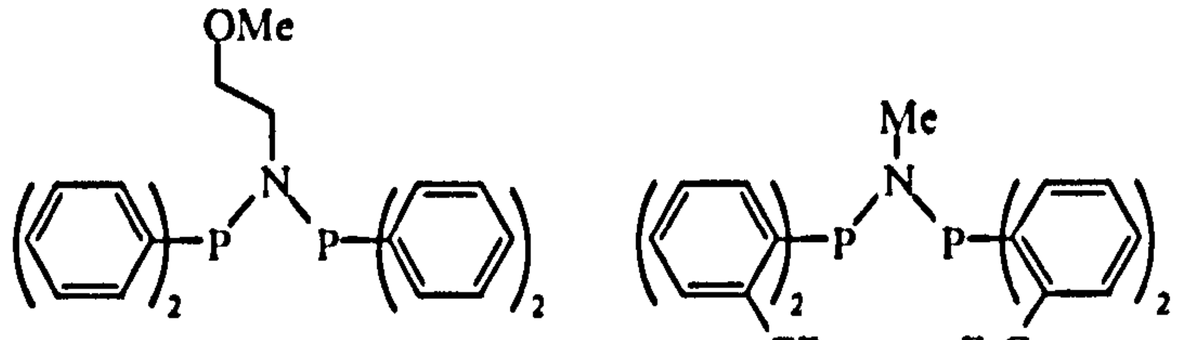
Table 2.15 – Cotrimerisation with PNP Ligands in Figure 2.11

Run	Ligand	Productivity / g (g Cr h)$^{-1}$	TOF of Cotrimer / h^{-1}	Cotrimers Product Distribution (wt %)						
				50	51	52	53-54	55-56	In 55-56 Fraction[a]	
									A	B
2.22	1	7926	2674	54.5	8.6	22.2	-	14.7	7.8	6.9
2.55	4	4863	1581	15.5	10.9	8.9	-	64.8	32.1	32.7
2.56	68	3077	1000	8.5	3.2	24.0	-	64.3	19.8	44.5
2.57	69	0	0	-	-	-	-	-	-	-

[a] Calculated as a percentage of whole cotrimer product and not as percentage of 55-56 fraction,

Ligand **4**, in run 2.55 in Table 2.15, is the *para* substituted analogue of **1**. A TOF of 1581 h^{-1} was obtained, with a selectivity of 64.8 % to cotrimer isomer **55** and **56**, whereas **1** is selective towards cotrimer isomers **50 – 52**. It seems that the OMe effect is not simply electronic and it is important to have this group in the *ortho* position for selectivity towards cotrimer isomers **52 - 54**. Ligand 68 (run 2.56 in Table 2.15) shows similar productivity and selectivity as ligand **4**, suggesting that the slightly better donor properties and reduced steric bulk of an OMe group is essential in achieving the observed unique selectivity for this derivative. Clearly the structural parameters affecting selectivity are extremely subtle. Ligand 69 (run 2.57 in Table 2.15) was found to be inactive towards cotrimerisation, this may be due to the bulky acetal groups being too bulky, or a change in coordination mode may be observed, as previously reported by Bercaw and co-workers for PNP ligands with ortho SMe groups (Figure 1.5).[40]

The two PNP ligands shown in Figure 2.12 were also tested for ethene/styrene cotrimerisation, the productivities and selectivities obtained are shown in Table 2.16.[98]



13 **70**

Figure 2.12 – Other PNP Ligands Tested for Cotrimerisation

Table 2.16 – Cotrimerisation with Ligand in Figure 2.12

Run	Ligand	Productivity / g (g Cr h)$^{-1}$	TOF of Cotrimer / h^{-1}	Cotrimers Product Distribution (wt %)						
				50	51	52	53-54	55-56	In 55-56 Fraction[a]	
									A	B
2.22	1	7926	2674	54.5	8.6	22.2	-	14.7	7.8	6.9
2.58	13	1758	574	2.9	4.2	9.0	-	83.9	46.0	38.0
2.59	70	0	0	-	-	-	-	-	-	-

[a] Calculated as a percentage of whole cotrimer product and not as percentage of 57 - 58 fraction,

The system using ligand **13** (run 2.58 in Table 2.16), in which there is the possibility of OMe donation *via* the nitrogen substituent, produced a TOF of 574 h^{-1} and had a selectivity to cotrimer isomer **55** and **56** of 83.9 %. Ligand **70** (run 2.59 in Table 2.16) has electron withdrawing group CF_3 groups in the *ortho* position and is inactive towards cotrimerisation. An electronic and steric effect is the possible cause of this result. It should be noted that this derivative also gives very poor results for ethene homo-oligomerisation.

From the range of ligand tested, **1**, is the only PNP to show a high selectivity (84 %) to isomers **50 - 52**. The remaining ligands that produced cotrimers showed a selectivity towards 3-phenylhexene **55 – 56**, with these isomers contributing to over 95 % of the total products for ligand **4**. Referring to Scheme 2.9 for ligand **1**, it seems insertion into the more hindered site of the common metallacyclopentane intermediate **58** is disfavoured. This is because the OMe on the PNP ligand can act as a pendant ligand to

the metal, increasing the bulk on the metal centre. In turn this leads to the formation of cotrimer isomers **50** to **52** over **55** and **56**. Insertion into the more hindered site is possible on systems where the ligand does not act as a tridentate system, producing cotrimer isomers **55** and **56**.

A further explanation for the selectivity towards cotrimers **55** and **56** for other PNP ligands may be due to the flexibility of the ligands. In **1** the OMe group is weakly coordinating, reducing rotation of the phenyl rings so this system is selective towards cotrimers **50** to **52**. In other *ortho* substituted ligands the other groups can rotate away from the metal centre reducing the effective steric bulk around the metal centre.

At 1 bar of ethene, the ligand systems in this section, other then **1**, have been shown be inactive for ethene trimerisation.[1, 4, 5] Therefore as expected, all systems which produced cotrimers gave a selectivity of 100 % towards cotrimers products and no 1-hexene was produced.

2.4.3.2. Bis(diarylphosphino)alkane Ligands for Cotrimerisation of Styrene and Ethene

Bis(diphenylphosphino)ethane, dppe, **71** was previously found, by Bollmann and co-workers, to be active for ethene tetramerisation albeit with inferior performance to PNP ligands.[55] Dppe and a range of derivatives were tested for styrene and ethene cotrimerisation, as shown in Figure 2.13.

Ligands **71** to **73** were synthesised using a modified literature procedure.[33, 41, 47, 99] The synthesis of these ligands is explained further in Chapter 5 along with the synthesis and characterisation of novel ligands **75** to **77**. The ligand systems where cotrimerisation occurred are shown in Table 2.17.

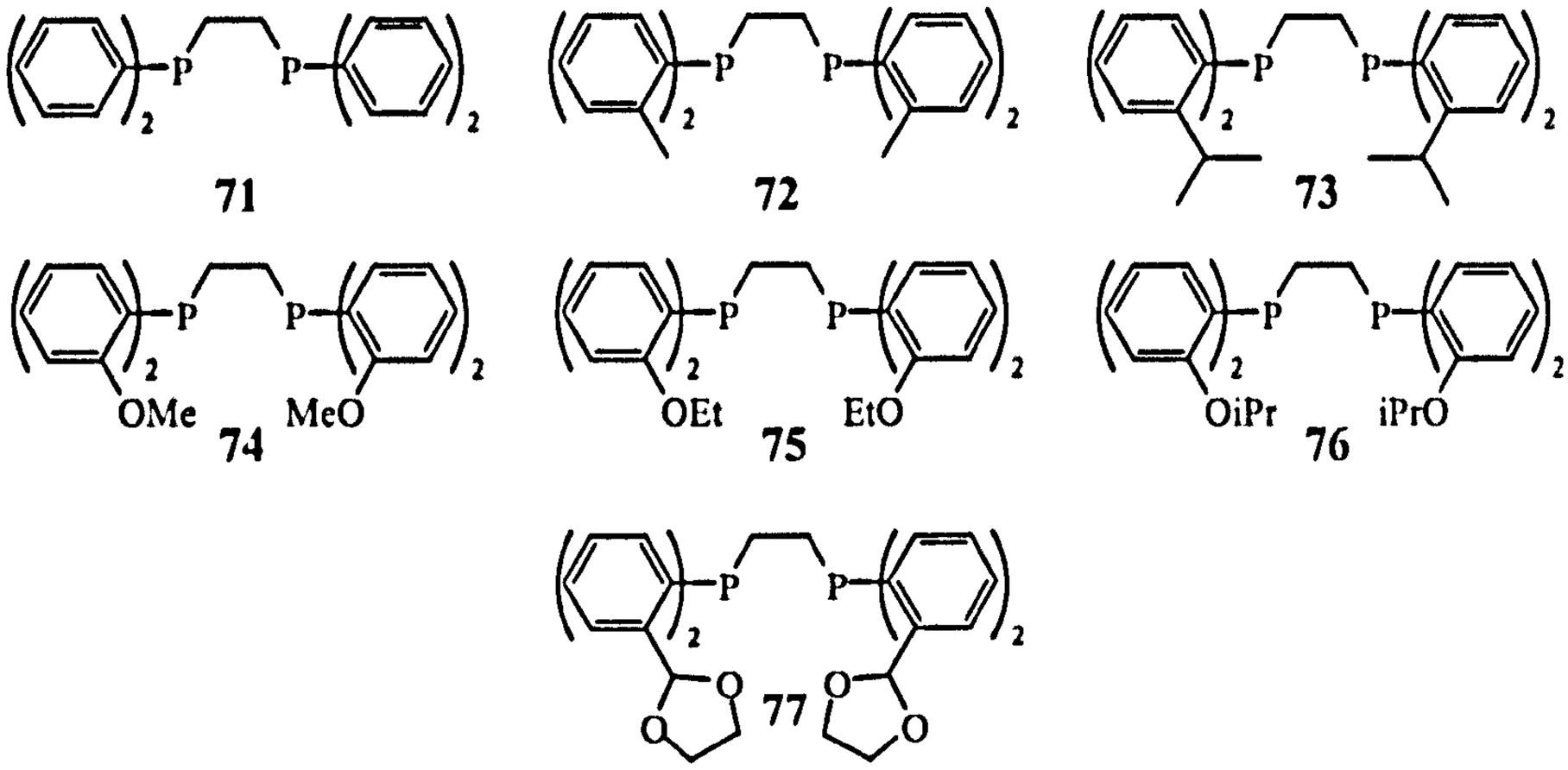


Figure 2.13 - Bis(diarylphosphino)ethane Ligands Tested for Cotrimerisation

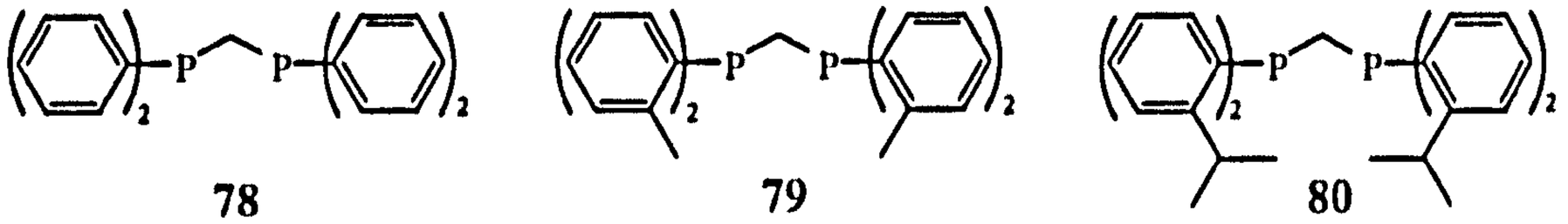
Table 2.17 – Cotrimerisation Results for Ligands in Figure 2.13

Run	Ligand	Productivity / g (g Cr h)$^{-1}$	TOF of Cotrimer / h^{-1}	Cotrimers Product Distribution (wt %)						
				50	51	52	53-54	55-56	In 55-56 Fraction[a]	
									A	B
2.22	1	7926	2674	54.5	8.6	22.2	-	14.7	7.8	6.9
2.60	71	495	164	20.9	4.7	6.1	-	68.3	37.4	30.9

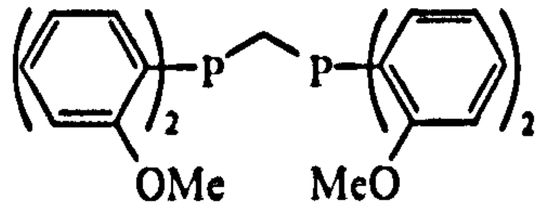
[a] Calculated as a percentage of whole cotrimer product and not as percentage of 57 - 58 fraction,

Dppe, **71** (run 2.60 in Table 2.17) was found to give a low TOF of 164 h^{-1} with the products consisting of 68 % cotrimer isomers **55** and **56**. A range of *ortho* substituted derivatives of dppe, as illustrated, were tested but found to be inactive towards cotrimerisation.

A range of derivatives of bis(diphenylphosphino)methane, dppm, were also tested for cotrimerisation and are shown in Figure 2.14. The ligands were synthesised using the same method as the dppe derivatives, using a modified literature method.[33, 41, 47, 99]



78 **79** **80**



75

Figure 2.14 - Bis(diarylphosphino)methane Ligands Tested for Cotrimerisation

These ligands were also found to be inactive for cotrimerisation. Dppm derivatives are also inactive towards ethene trimerisation, where it is believed that the carbon in the backbone is deprotonated during catalyst activation, causing catalyst deactivation. Increasing the temperature to 70 °C had no effect on the activity.

With only PNP ligands showing activity towards styrene and ethene trimerisation, and other ligands being inactive, it seems that the backbone of the ligand plays a crucial part in catalysis.

2.5. Summary

$[CrCl_3(thf)_3]$/PNP/MAO systems have previously been shown to be highly active towards ethene trimerisation, with the $[CrCl_3(thf)_3]$/**1**/MAO system showing the best results and a productivity of 1,033,000 g (g Cr h)$^{-1}$. This $[CrCl_3(thf)_3]$/**1**/MAO system was tested for the cotrimerisation of styrene and ethene and was found to form cotrimers consisting of one styrene and two ethene units, which were isomers of phenylhexene. With 0.02 mmol of $[CrCl_3(thf)_3]$, 0.02 mmol of **1**, 300 equivalents of MAO, a styrene concentration of 6.0 mol dm^{-3}, at 25 °C and with a run time of 1 h, a TOF of 2468 h^{-1} was obtained, with a selectivity to the cotrimer products of over 95 %. A selection of results from this chapter has been published.[93]

The possible isomers of phenylhexene produced could be determined from the postulated mechanism, which was adapted from the well established mechanism for the trimerisation of ethene.[4] Firstly either two ethene or one ethene and one styrene

molecule coordinate to the metal centre and oxidatively couple to give a substituted chromacyclopentane. This is followed by insertion of the either styrene or ethene to give chromacycloheptane. β-hydride elimination followed by reductive elimination occurs to give seven different isomers of phenylhexene, (*E/Z*)-1-phenyl-1-hexene, **50**, **51**, 6-phenyl-1-hexene, **52**, 2-phenyl-1-hexene, **53**, 5-phenyl-1-hexene, **54**, 4-phenyl-1-hexene, **55** and 3-phenyl-1-hexene, **56**. From comparison of the cotrimer products with the ^{13}C NMR and GC data of standards, it was found that the cotrimer mixture consisted of cotrimer isomers **50 - 52**, **55** and **56**. Isomers **53** and **54** were not present, which suggested that, in the mechanism styrene inserts *via* a 2,1 regiochemistry, where the phenyl ring interacts with the metal centre. The $[CrCl_3(thf)_3]$/**1**/MAO system showed a selectivity to isomers **50 – 52** of 84.9 %. The factors affecting selectivity are very subtle and a full rationale remains elusive at this point.

The effect of changing the reaction conditions was investigated. It was found that as the temperature of reaction was increased the overall productivity and cotrimer selectivity were decreased. The cotrimer selectivity was increased upon increasing the styrene concentration, although the productivity decreased. Also it was found that changing the ligand, changed the selectivity to cotrimer isomer **55** and **56**, with a system using ligand **19** showing selectivity towards **55** and **56** of 95.1 %. Ligand **1** was the only ligand to show selectivity to cotrimer isomers **50 – 52**.

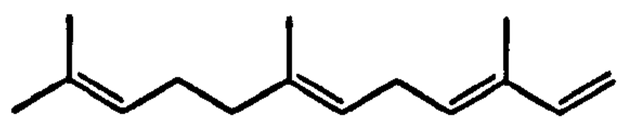
Chapter 3

Trimerisation of 1,3-Dienes

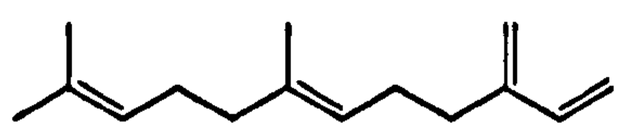
3.1. Introduction

Oligomerisation of 1,3-dienes has generated a significant amount of interest as an attractive direct route to such compounds as isoprenoids or terpenoids.[100] Isoprenoids are oligomers of isoprene, which are found in many essential oils and are extensively used in traditional and herbal medicines, perfumes, aromatherapy oils and as flavour additives in food. Terpenes are derived from isoprenoids and are commonly found in nature, for example, in conifer wood, citrus fruits, eucalyptus, roses, rosemary, sage and thyme. As well as plant life, insects can metabolise terpenes to form pheromones. This shows the importance and extensive usage of isoprene oligomers and demonstrates the significance of research into syntheses of these compounds.

Farnesene is the collective name of a group of terpenoids commonly found in nature. Two examples, shown in Figure 3.1, are α-farnesene (3,7,11-trimethyl-1,3,6,10-dodecatetraene), which is found in the coating of apples and *trans*-β-farnesene (7,11-dimethyl-3-methylene-1,6,10-dodecatriene), a constituent of essential oils and an intermediate in the synthesis of many sesquiterpenoids and diterpenoids, for instance farnesylacetone and squalene.



α-(E,E)-Farnesene
82



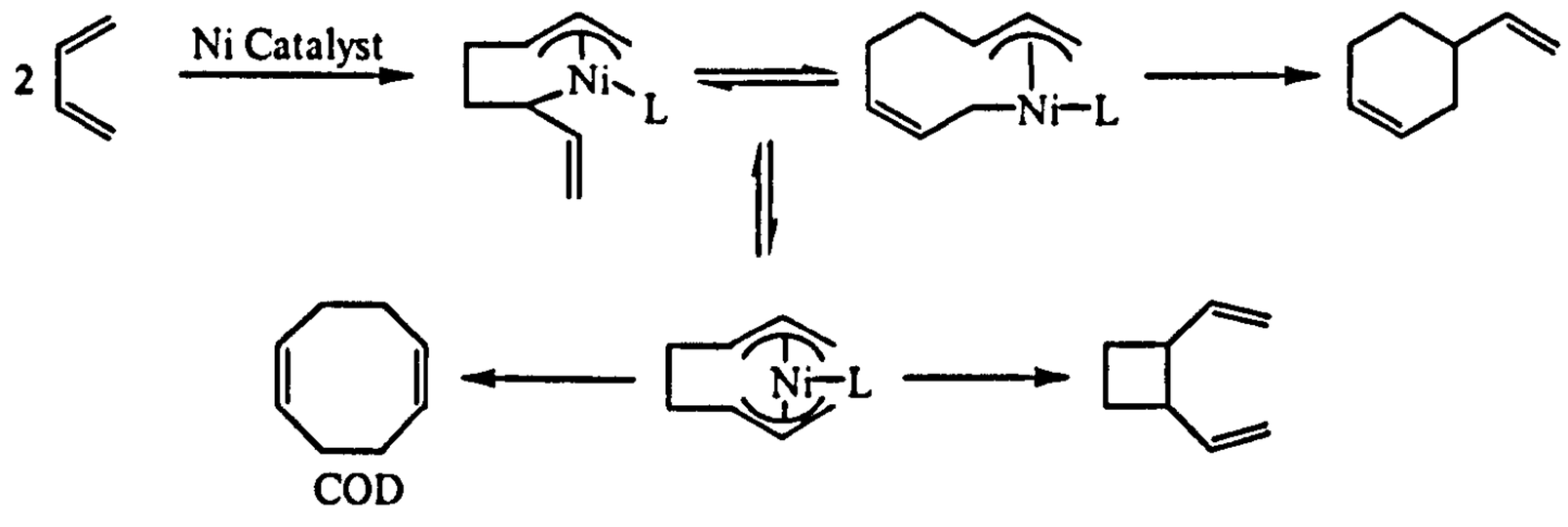
ß-(E)-farnesene
83

Figure 3.1 – Isomers of Farnesene

With a large commercial market for these compounds, there is a need for research into methods for selectively synthesising terpenoids. A great deal of research has been carried out on dimerisation of 1,3-dienes,[100-102] but there is very little research on selective trimerisation.[103-108]

3.1.1. 1,3-Butadiene Dimerisation and Trimerisation

The cyclo-dimerisation of 1,3-butadiene is a well-known process, with 1,5 cyclooctadiene (COD) and vinylcyclohexene being the main products, 1,2-divinylcyclobutane can also be produced, see Scheme 3.1. Nickel phosphine catalysts have been shown to be highly effective for butadiene cyclo-dimerisation, although the ratio of each product depends greatly on the conversion of butadiene and the electronic properties of the ligand.[109] The mechanism will be explained further in Section 3.1.4.[92]

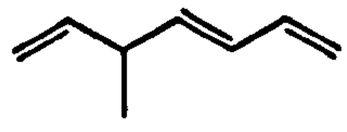
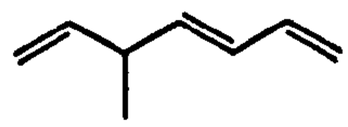
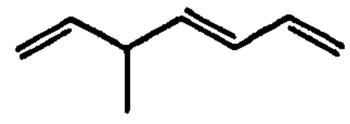
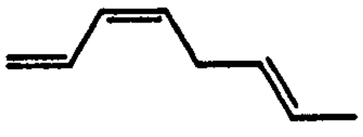
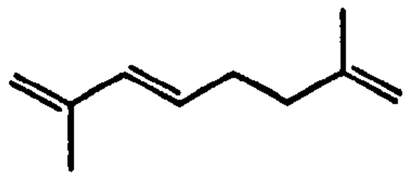
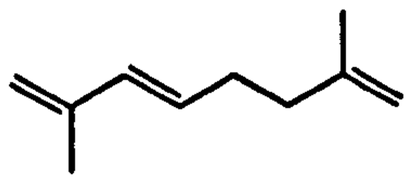
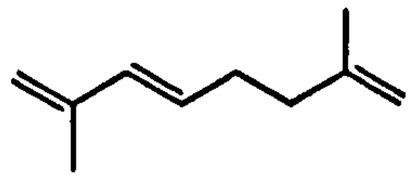


Scheme 3.1 – Cyclodimerisation of Butadiene

A zerovalent 'bare' nickel complex such as [Ni(COD)$_2$] is used.[85, 110] If the ligand tested is tri(cyclohexyl)phosphine, the selectivity is 40 % vinylcyclohexene, whereas for tris(2-biphenylyl) phosphate, the selectivity is towards 1,5-cyclooctadiene (97%). It has been found that going from butadiene to isoprene and then to 2,3-dimethyl-1,3-butadiene, thus increasing the number of methyl groups, causes a decrease in the selectivity towards cyclooctadiene derivatives, 1,5-dimethylcyclooctadiene (from isoprene) and 1,2,5,6-tetramethylcyclooctadiene (from 2,3-dimethyl-1,3-butadiene) and increases the selectivity towards vinylcyclohexene derivatives.[111] Iron complexes, such as diethylbis(dipyridyl)iron[112] and $FeCl_3/PPh_3/AlEt_3$[113] have also been shown to be active towards butadiene cyclo- and linear dimerisation.

Table 3.1 shows a selection of results from catalysts used for the linear dimerisation of 1,3-butadiene and isoprene.[111]

Table 3.1 – Linear Dimerisation of 1,3-Dienes

1,3-Diene	Catalyst System	Yield / %	Product Distribution	
			Product	Selectivity / %
1,3-Butadiene	$[Co(\eta^3\text{-}C_3H_5)_3]$	93		100
	$[Co(acac)_3]$ + BuLi	77		65
			Trimers	35
	$[FeCl_3]$ + PPh_3 + $AlEt_3$	85		30
				65
			Trimers	5
Isoprene	$[Pd(MaAn)_2(PPh_3)_2]$	[a]		100
	$[TiCl_4]$ + AlR_3	[a]	 + cyclodimers	43
			Trimers	39
			Tetramers	9
			Polymer	9
	$[VO(OEt)_3]$ + $AlClEt_2$	90		50
			Trimers and higher oligomers	15

BuLi – Butyl lithium; MaAn – Maleic Anhydride; [a] not reported.

It can be seen from Table 3.1 that the system using $[Co(\eta^3\text{-}C_3H_5)_3]$ is reported to have a selectivity of 100 % towards *trans*-3-methyl-1,4,6-heptatriene, whereas the selectivity towards dimers is reduced in the two systems using $[Co(acac)_3]$ and $[FeCl_3]$, with the observation of trimers and higher oligomers.[111] A similar trend is observed for the

linear dimerisation of isoprene. The system using $[Pd(MaAn)_2(PPh_3)_2]$, where MaAn is maleic anhydride, shows a selectivity to 2,7-dimethyl-1,3,6-octatriene of 100 %, whereas trimers, higher oligomers and polymer are observed in the systems using $[TiCl_4]$ and $[VO(OEt)_3]$.

In 1975 Takasago Perfumery Company developed palladium catalysts in order to dimerise substituted butadiene monomers, including isoprene, myrcene, and farnesene.[114] The catalyst system consisted of a palladium salt, of the formula $[PdX_2]$ (X is a halogen, NO_3, CN or $-OCOCH_3$) or a palladium π-allyl complex, with the structure shown in Figure 3.2. Phosphines or arsines were used as the ligands, with the formula PR_3 or AsR_3, where R is an aromatic or alkyl group.

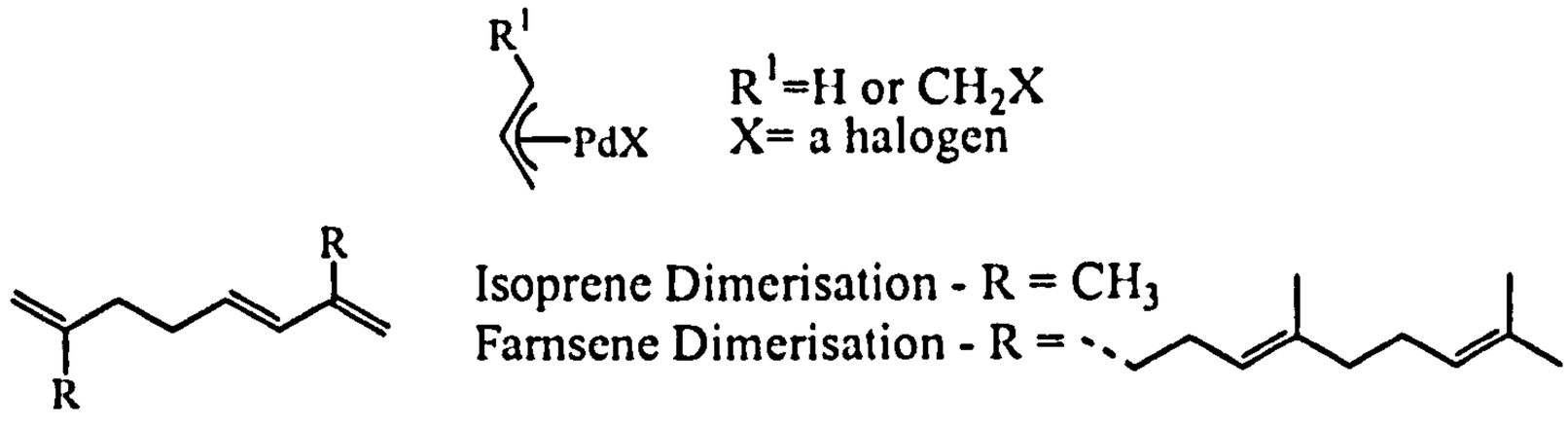
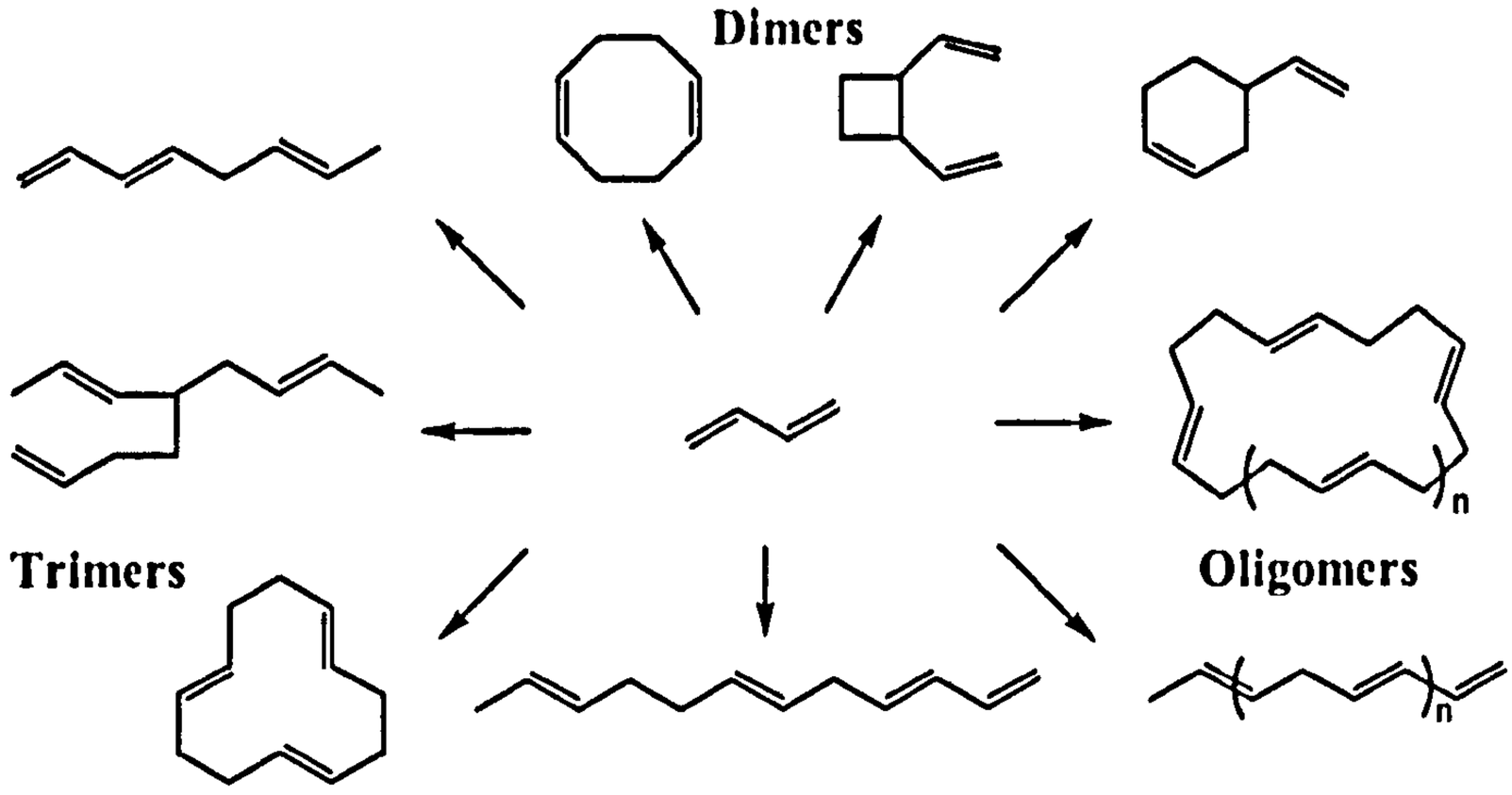


Figure 3.2 – Dimerisation of Isoprenoids

Squalene type hydrocarbons are formed from the dimerisation of farnesene (Figure 3.2), which are then used as a raw material for cosmetics and machine oils. Naturally occurring squalene was obtained by hydrogenation with Raney-Nickel under H_2 at 150 °C.[114]

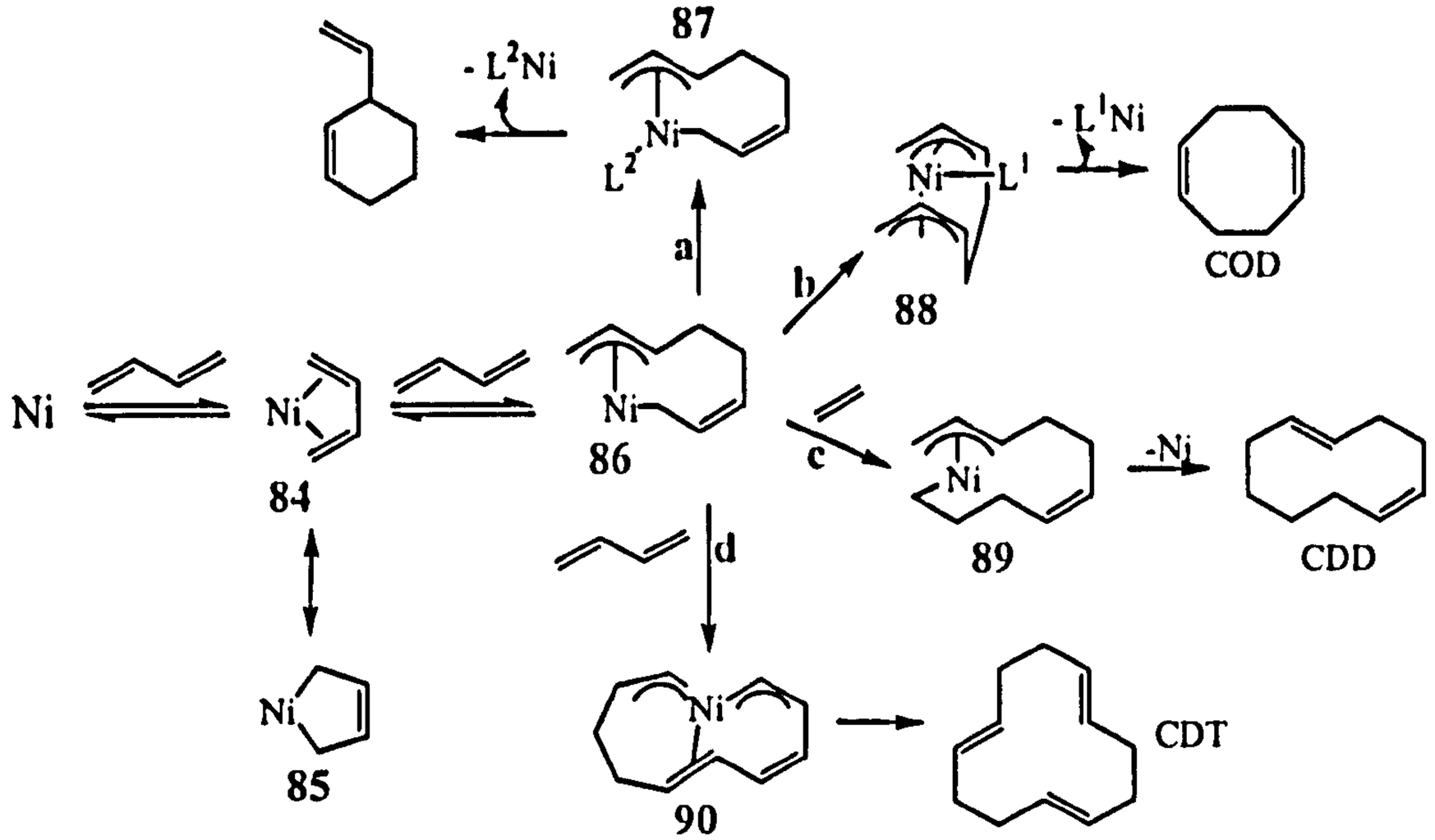
The trimerisation of 1,3-butadiene was first reported by Reed in 1954, with Wilke reporting the first practical synthesis of cyclododecatriene (CDT) in 1957.[115, 116] 1,5,9-Cyclododecatriene is produced in large quantities and used as the starting material for synthesising lauryl lactum and dodecanoic acid, which in turn are used to make polyamides, such as Nylon. As with 1,3-butadiene dimerisation, trimerisation uses Ni-allyl catalysts, formed from 'zero valent' Ni complexes such as $[Ni(COD)_2]$. The switch from dimerisation to trimerisation depends on the ligand, a variety of possible products are shown in Scheme 3.2.[117]



Scheme 3.2 – Products from the Trimerisation of Butadiene

Scheme 3.2 shows than range of products that can be obtained from the oligomerisation of butadiene, with linear and cyclic product obtainable.[117] The products depend greatly on the reaction conditions, for trimerisation small ligands are needed so the coordination sphere can accommodate three butadiene units but if phosphine ligands are added then dimerisation occurs.[118] A small change in the catalytic system can change the selectivity of the products from dimers to trimers and oligomers, showing the versatility of the system.

1,3-Dienes are able to undergo homo-oligomerisation *via* photochemical reactions,[119] anionic methods[120] and metallacycles.[117, 120] The products obtained depends on the mechanism of the catalyst, with linear and cyclic products possible. Scheme 3.3 shows examples of possible dimers, trimers and oligomers from the oligomerisation of butadiene to cyclic products.[117]



Scheme 3.3 – Mechanism for Cyclodimerisation, Cyclotrimerisation of 1,3-Butadiene and the Cyclo-cotrimerisation of 1,2-Butadiene with Ethene

Scheme 3.3 shows the mechanism for the cyclodimerisation (route **a** and **b**), cyclotrimerisation (route **d**) of 1,3-butadiene and the cyclo-cotrimerisation of 1,3-butadiene with ethene (route **c**). When nickel phosphine complexes are used as the catalysts, the products obtained are greatly dependant on the ligand used. As previously stated there are three main products obtained from the dimerisation of butadiene, which are cyclooctadiene (COD), methylcyclohexene and divinylcyclobutane. The mechanism goes *via* a zero valent 'bare' nickel, then 1,3-butadiene coordinates to the 'bare' nickel. This then undergoes oxidative addition to give metallacyclopentane **85**, which is analogous to the chromacyclopentane intermediate seen in the trimerisation of ethene. Next a second butadiene monomer inserts into intermediate **84** or **85** to give Ni-allyl species **86**, this is the common intermediate in the dimerisation, trimerisation and cotrimerisation of butadiene. For butadiene dimerisation, the final product depends on the Ni-allyl species formed from intermediate **86** and this is governed by the electronic and steric properties of the phosphine ligand. If route **a** is taken, where a bulky phosphine is used, then reductive elimination of **86** occurs to give **87** then

vinylcyclohexene. For electron donating or less bulky phosphines, route **b** is observed, where intermediate **86** undergoes rearrangement to form the di-π-allyl-Ni species, **88**, which then undergoes reductive elimination to give 1,5-cyclooctadiene (COD). For trimerisation a third butadiene monomer inserts into intermediate **86** to give route **d**. A C_{12} Ni-diallyl species, **90**, is formed, which undergoes reductive elimination to give 1,5,9-cyclododecatriene (CDT). Route **c** shows cotrimerisation of butadiene with ethene, where the insertion of ethene into intermediate **86** gives a C_{10} Ni-allyl intermediate, **89**, followed by reductive elimination to give 1,5-cyclodecadiene (CDD).

3.1.2. Isoprene Dimerisation and Trimerisation

Dimerisation of isoprene is also known using hafnium[122], cobalt[123], iron[123] and zirconium[124]. A selection of results is shown in Table 3.2.

Table 3.2 – Oligomerisation of Isoprene[128 - 130]

Catalyst Precurser (Catalyst:isoprene ratio)	Solvent, Activator, Ligand	Conversion / %	Product Distribution / %	
			Dimer	Trimer
$[Fe(acac)_3]$ (1:100)	Bipyridine $AlEt_3$, 90 °C	100	92	Not Given
$[Hf(OBu)_4]$ (1:100)	$AlClEt_2$ Benzene, 130 °C	45	20[a]	0
$[Zr(OBu)_4]$ (1:100)	$AlClEt_2$ Benzene, 100 °C	100	50	20

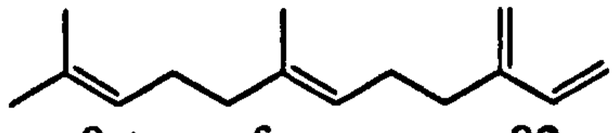
[a] mainly higher oligomers.

Wilke extended the investigation to isoprene and found that isomers of trimethylcyclododecatriene were formed, along with a linear isoprene dimer.[109] Morikawa and co-workers investigated isoprene dimerisation and trimerisation, with Ziegler type systems. A system consisting of $[TiCl_4]$, $AlClEt_2$ and a cyclic ether, dimerised isoprene, giving 2,4-dimethyl-4-vinylcyclohexene and 2,6-dimethyl-1,3,6-octatriene, with the ratio depending on the ligand. Linear isomers, including 2,6,10-trimethyl-1,3,6,11-dodecatetraene, 2,7,11-trimethyl-1,3,6,11-dodecatetraene, **92**, and cyclic trimers were produced by a Ni system using nickel octoate, $AlEt_3$ and

phosphites. The structure of the trimers depended on the basicity of the ligands and as the bulkiness of the ligand decreases the selectivity towards trimers increases, as three isoprene monomers can coordinate to the metal centre.[125]

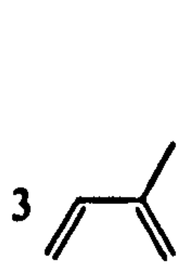
In 1977 and 1980 Mitsubishi Petrochemical Company filed patents on the trimerisation of isoprene using trivalent titanium halogen complexes with aromatic aldehyde groups such as $[Ti(C_6H_5CHO)_2Cl_3]$ and nickel complexes, such as $[Ni(acac)_2]$.[126, 127] Organoaluminium compounds were used as catalyst activators. Both of these systems formed mainly cyclic trimers, with a high selectivity to 1,5,9-trimethylcyclo-dodecatriene.

Akutagawa and co-workers developed nickel isoprene trimerisation catalysts forming linear isoprene trimers, as shown in Scheme 3.4.[103, 128]



β-trans-farnesene – 82

+

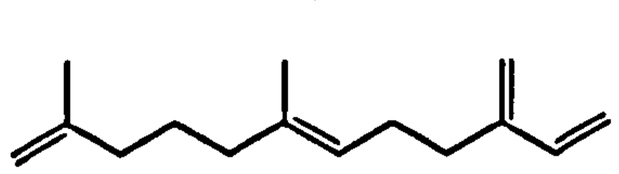


3

Ni Catalyst

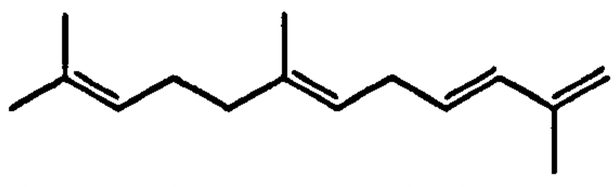
50 °C, 10 h

2 mol % Ni to isoprene



2,6-dimethyl-10-methylene-
1,6-*trans*-11-dodecatriene - 91

+



2,7,11-trimethyl-1,3,6,11-dodecatetraene - 92

Scheme 3.4 – Trimerisation of Isoprene Using Ni Catalysts

Table 3.3 shows results obtained by Akutagawa and co-workers in the trimerisation of isoprene.[103, 128]

Table 3.3 – Catalyst Results from Ni Catalysts Developed by Akutagawa and Co-workers

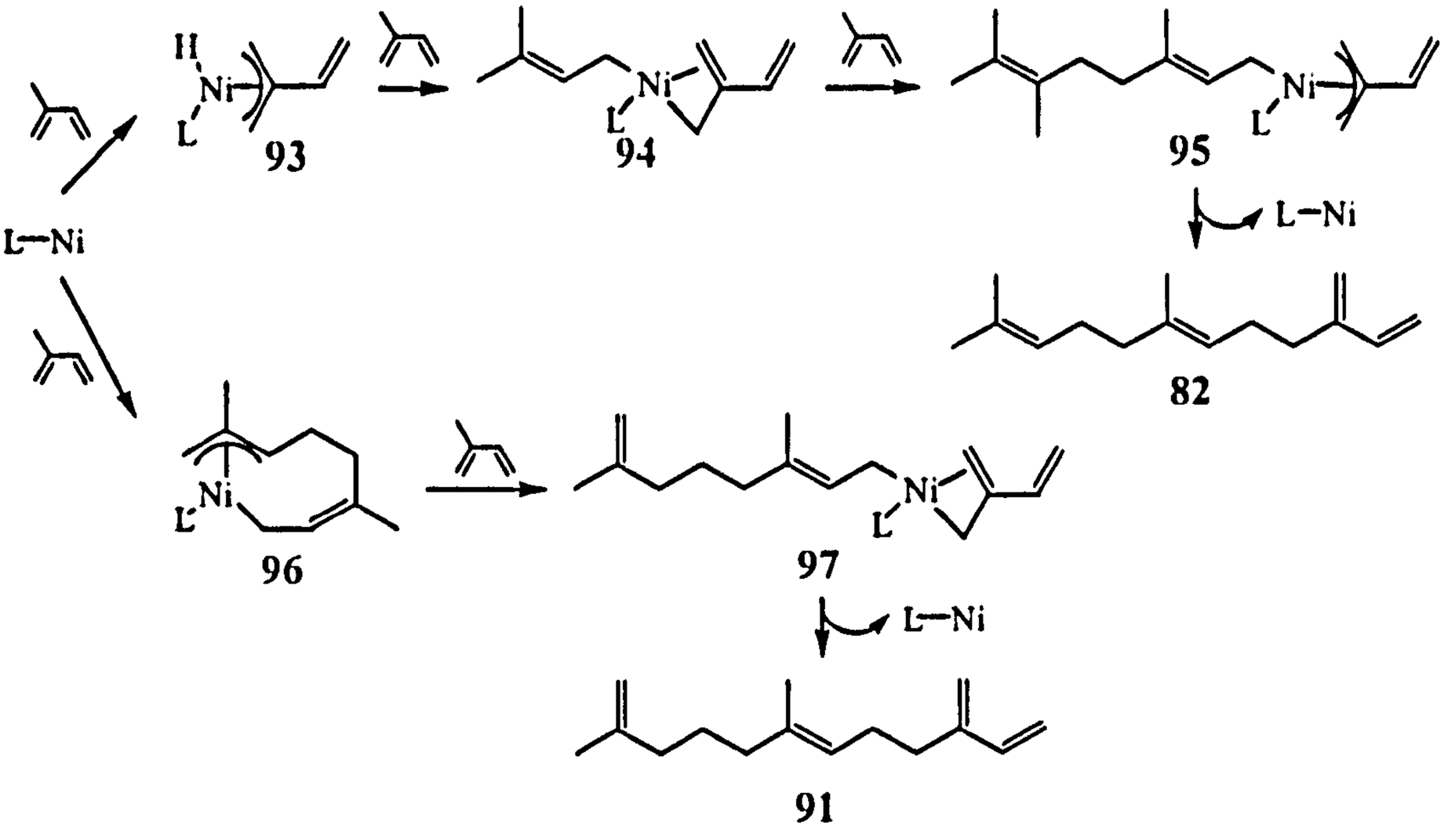
Run	Ni Precatalyst System	Prod. / g (g Ni h)$^{-1}$	Product Distribution / %					
			Dimers[c]	Trimers				C_{20+}
				Total	82	91	92	Cyc.
3.1[a]	[Ni(η^3-C_3H_5)], $PPh(NEt_2)_2$	2	12	85	1	71	[d]	3
3.2[a]	[Ni(acac)$_2$], PPh_3, Et_3Al	6	21	73	3	22	41	7	6
3.3[b]	[NiBr(η^3-C_3H_5) ($PPh(NEt_2)_2$], *n*-$C_{15}H_{31}ONa$	4	21	58	[d] predominantly **82** and **91**				21

[a] 2 mol % Ni to isoprene used, 50 °C, 10 h, ref. 128; [b] 1 mol % Ni to isoprene, 70 °C, 7 h, ratio base to catalyst is 2:1, ref. 103; [c] dipentene, 1,5-dimethyl-5-vinyl-1-cyclohexene and 1,5-dimethyl-1,5-cyclooctadiene; [d] not reported.

The group found that three trimer isomers were obtained, as shown in Scheme 3.4, the selectivity depended on the catalyst with the [Ni(acac)$_2$] system having a higher selectivity to isomer **92** of 41 % (run 3.2 in Table 3.3) and the [Ni(η^3-C_3H_5)] system having a higher selectivity to isomer **91** of 71 % (run 3.1 in Table 3.3).[128] In 1978 the group reported further investigations, where it was shown that the electronic properties of the ligands have a profound effect on the catalysis, with electron donating phosphines and arsines needed for efficient catalysis. Mononuclear halide complexes were ineffective, although if the halide is replaced with an alkoxide group, linear trimers **82** and **91** are produced. The role of the alkoxide is to stabilise hydrogen abstraction from the hydride species formed in the catalytic cycle. There is a balance between getting a high conversion and producing the desired isomers **82** and **91**, with a high conversion coming at the expense of selectivity to these isomers.[103]

Dzhemilev and co-workers investigated Ni borate complexes.[129] The system with [Ni(acac)$_3$], B(OC_4H_9)$_3$ and $AlEt_3$, at 80 °C, gave a mixture of dimers and trimers, with an 87 % yield and a selectivity of 45 % to dimers, 50 % trimethyl-1,5,9-cyclododecatriene and 5 % 2,6,10-trimethyldodecatetraene. Tetramers and higher oligomers were also seen.

Akutagawa and co-workers proposed a mechanism for the trimerisation of isoprene using Ni catalysts. The proposed mechanism is given in Scheme 3.5.[103]



Scheme 3.5 – Trimerisation of Isoprene using a Ni-allyl Catalyst

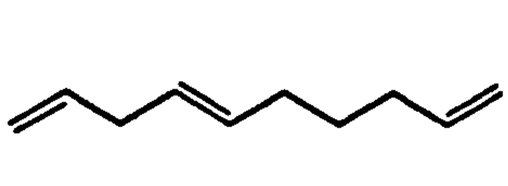
The group found that the two main trimer products were linear isomers **82** and **91**.[103, 128] It was reported that as the Ni catalytic system used was unable to isomerise **82** to **91** then two routes must be competing to form the two isomers. In the first route, an isoprene monomer coordinates to the Ni centre and hydrogen migration occurs, forming η^3-allyl species **93**. This is the least hindered and most stable η^3-allyl species possible from the coordination of isoprene, as it contains a tertiary carbon. A second isoprene monomer inserts into the Ni-H bond to give **94**, this is followed by the insertion of a third isoprene monomer to give species **95**. Finally reductive elimination occurs to give isomer **82** and regenerate the catalyst. It is important to state that although this mechanism appears to be selective towards trimer products, the mechanism is an insertion/elimination mechanism and so a Schultz Flory distribution is still seen. The selectivity towards trimer products is due to the rate of elimination being higher than the rate of insertion of the fourth isoprene monomer.

The second route follows the formation of intermediate **96** from the coordination and oxidative coupling of two isoprene monomers. The next step is the coordination of a

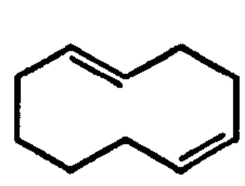
third isoprene monomer, along with nucleophillic hydride attack on the secondary carbon in the η^3-allyl group in intermediate **96**, giving **97**. Reductive elimination then occurs to give isomer **91**. This mechanism does not take into account the formation of cyclic trimers, suggesting that other intermediates, similar to the intermediates seen in the cyclotrimerisation of butadiene are also involved.

3.1.3. Background to Co-oligomerisation

Wilke reported that adding ethene to the nickel allyl butadiene trimerisation/dimerisation systems can cause co-oligomerisation to occur.[116] It was found that the presence of ethene reduces the productivity of butadiene trimers and ethene was incorporated into products. The products consisted of two butadiene units and one ethene unit, giving cyclic and linear C_{10} compounds such as 1,5-cyclodecadiene and 1,4,9-decatriene. Co-oligomerisation is stereoselective, with *cis*-1-*trans*-5-cyclodecadiene and 1-*trans*-4,9-decatriene being the predominant products (Figure 3.3).[109, 110]



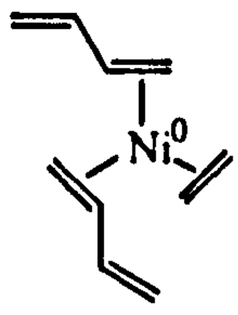
1-*trans*-4,9-decatriene



cis-1-*trans*-5-cyclodecadiene

Figure 3.3 – Product from Cotrimerisation of 1,3-Butadiene and Ethene

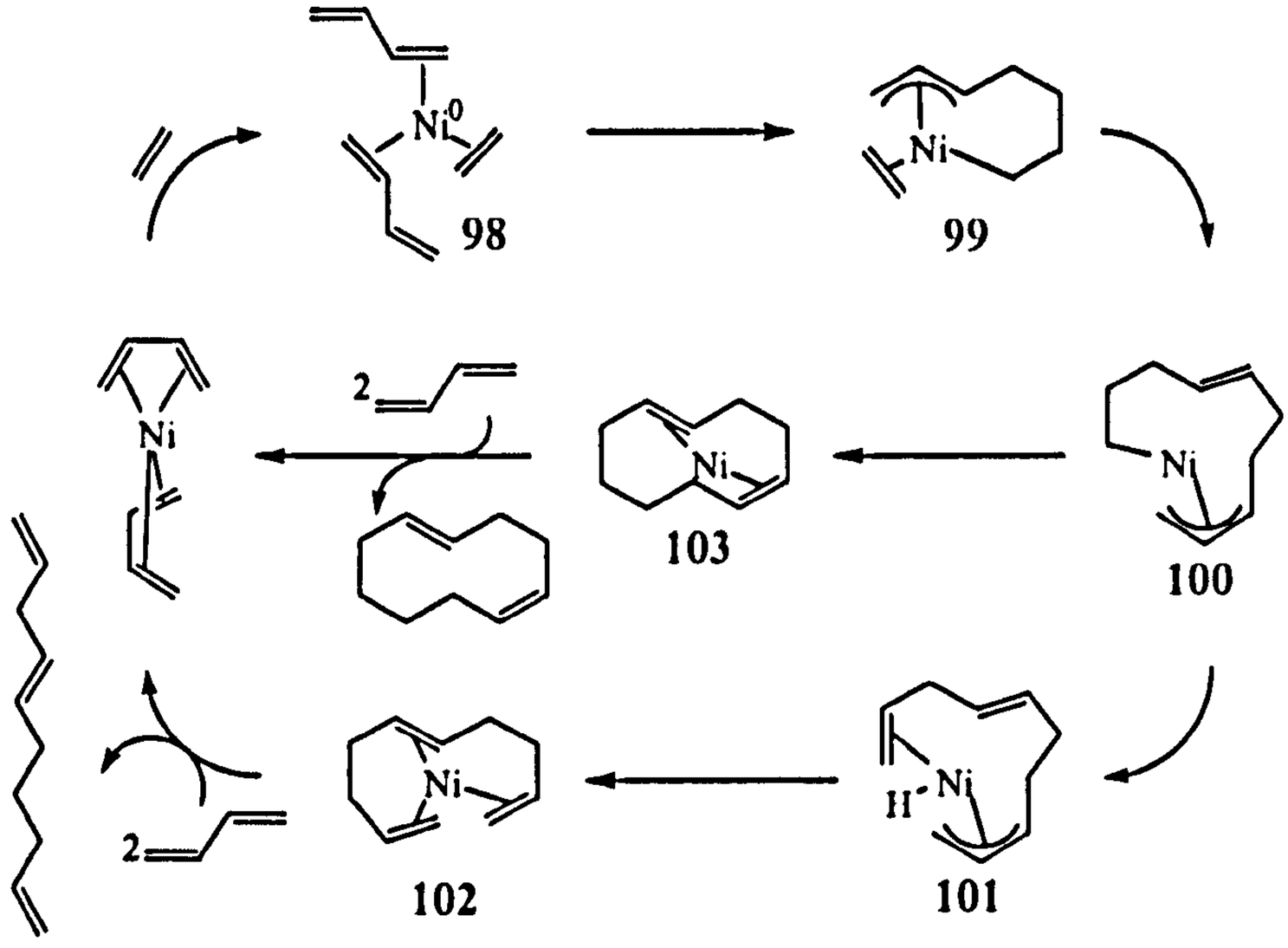
Tobisch investigated the competition between the generation of linear and cyclic C_{10} materials.[110] The mechanism goes *via* the formation of $[Ni^0(\eta^2\text{-}CH_2CH_2CH_2CH_2)_2(C_2H_4)]$ with the bis(η^2-*trans*) isomer being the most stable (Figure 3.4), therefore insertion of ethene causes butadiene to go from 1,4 insertion to 1,2 insertion.



$[Ni^0(\ 2\text{-}CH_2CH_2CH_2CH_2)_2(C_2H_4)]$

Figure 3.4 – Proposed Intermediate in Butadiene/Ethene Cotrimerisation

Scheme 3.6, gives the mechanism for the formation of the linear and cyclic C_{10} products, *cis*-1-*trans*-5-cyclodecadiene and 1-*trans*-4,9-decatriene.[110]

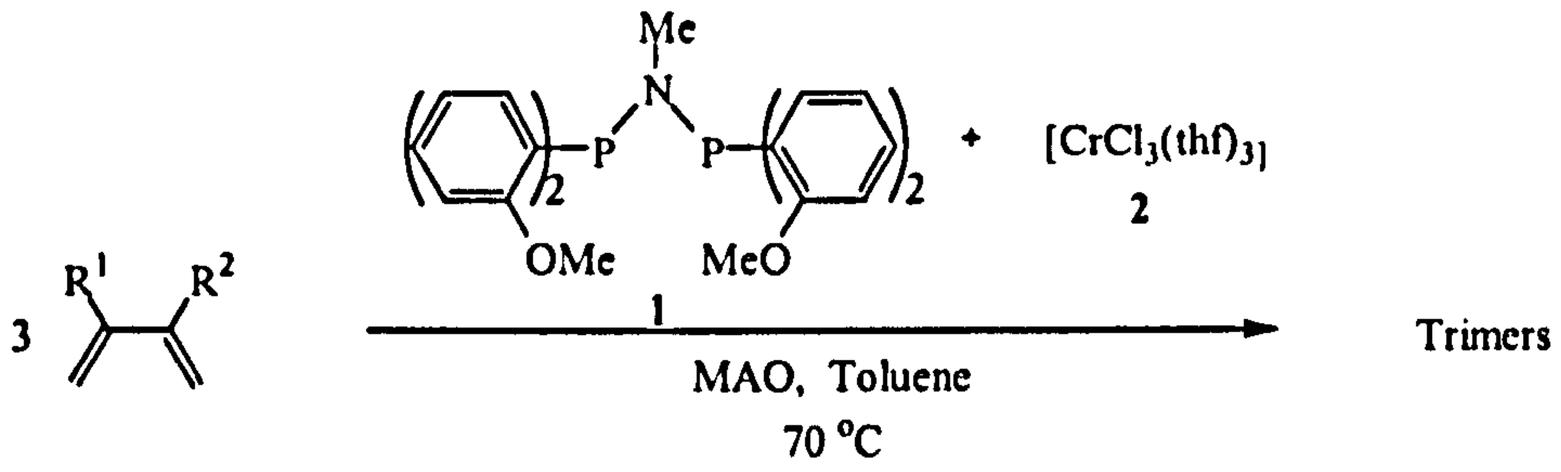


Scheme 3.6 – Cotrimerisation of Ethene and 1,3-Butadiene

After the formation of $[Ni^0(\eta^2\text{-}CH_2CH_2CH_2CH_2)_2(C_2H_4)]$, **98**, the mechanism continues *via* the oxidative coupling of the two butadiene units, forming a Ni-allyl species **99**, this is followed by the insertion of ethene to give the intermediate **100**. Intermediate **100** can then either undergo reductive elimination to give **103** then the cyclic product, or β-hydride elimination to give **101**, followed by reductive elimination to give the linear product.

3.2. Aim of Research

Chromium *N,N*-bis(diarylphosphino)alkylamine complexes have been shown to be highly active towards ethene trimerisation. One of the best systems, shown in Scheme 3.7, was developed by Wass and co-workers using ligand **1** as the ligand, $[CrCl_3(thf)_3]$ was used as the catalyst precursor, MAO as the activator and toluene as the solvent.[1, 4] In chapter 2 this system was shown to form 1-phenylhexene isomers from the cotrimerisation of ethene and styrene in high selectivity and productivity.[4, 93]



Butadiene - $R^1=R^2=H$
Isoprene - $R^1=Me$, $R^2=H$
2,3-Dimethylbuta-1,3-diene - $R^1=R^2=Me$

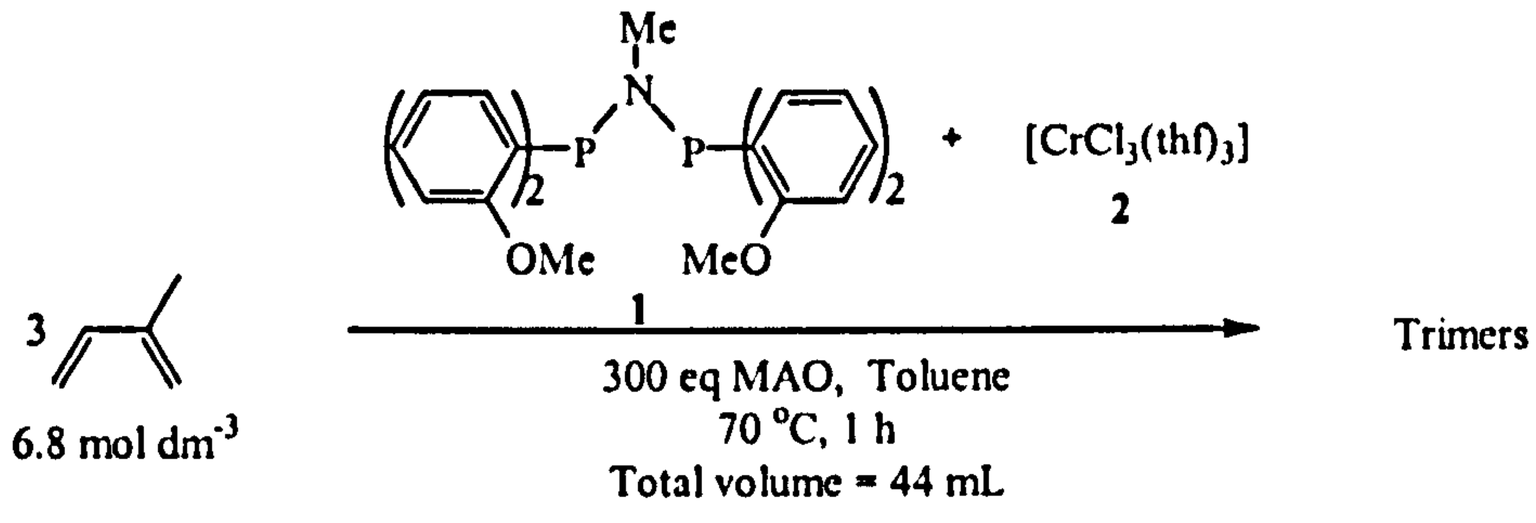
Scheme 3.7 – General Scheme for 1,3 Diene Trimerisation

The aim of this chapter is to investigate the use of chromium PNP complexes for the trimerisation of isoprene. This will include the identification of the products obtained, by NMR and gas chromatography (GC) and determining how the productivity and selectivity is affected by the reaction conditions, such as temperature, isoprene concentration, reaction time and the ligand used. The investigation will be extended to 1,3-butadiene and 2,3-dimethyl-1,3-butadiene.

3.3. Trimerisation of Isoprene

3.3.1. Standard Reaction Conditions and Methodology

The catalytic system shown in Scheme 3.8 was tested for the ability to trimerise isoprene. The method used for the trimerisation of isoprene was adapted from the literature method for using Cr PNP complexes to trimerise ethene and from using Ni-π-allyl complexes for the trimerisation of isoprene.[4, 93, 103, 62]



Scheme 3.8 – General Scheme for Isoprene Trimerisation

Unless otherwise stated, the standard conditions were: 0.02 mmol of $[CrCl_3(thf)_3]$, 0.02 mmol of ligand **1**, 300 equivalents of MAO, 6.8 mol dm^{-3} of distilled isoprene and toluene was used as the solvent. The reaction was completed at 70 °C and with a reaction time of one hour.[93, 103, 128] Under these conditions this system gave promising results, with selectivity of 79.9 % towards C_{15} products and a productivity of 826 g (g Cr h)$^{-1}$, which translates into a turnover frequency (TOF) of 660 h^{-1}. Previous reports of isoprene trimerisation by Akutagawa and co-workers, using a nickel catalyst only gave a TOF of between about 2 to 4 h^{-1} or productivities of between 2 to 6 g (g Cr h)$^{-1}$ and selectivities of 50 to 80 % towards isoprene trimer materials.[103, 131] The $[CrCl_3(thf)_3]$/**1**/ MAO system produced a TOF which is about 200 times better than that previously reported, with comparable selectivities.

3.3.2. Product Analysis and Identification

The GC data from the trimerisation of isoprene, using the system shown in Scheme 3.8, showed that the product mixture contain unknown compounds with a high boiling point (see Appendix 8.2 for the GC trace). The next stage was to identify these products. Initially the products were compared to the GC retention times of a range of commercially available *n*-alkanes, to determine whether the products were dimers or trimers. It was found that the products were isoprene trimers, which was also supported by GC-MS data. Therefore it was shown that the $[CrCl_3(thf)_3]$/1/MAO system was able to trimerise isoprene, with the GC trace containing four main trimer peaks and higher oligomer peaks.

3.3.2.1. Proposed Mechanism For Formation of Possible Isomers

As with the cotrimerisation of styrene and ethene (Chapter 2), the possible trimers could be predicted from looking at the proposed mechanism. This was adapted from that proposed for the Ni catalysed trimerisation of 1,3-butadiene and the trimerisation of isoprene, as described in Section 3.2.[85, 103, 128] It also takes into account the metallacycle mechanism proposed for the trimerisation of ethene using Cr catalysts.[1, 4] The mechanism for the trimerisation of 1,3-dienes is proposed to go *via* metal-allyl species, as shown in Scheme 3.9.[111] The labelling system for isoprene used in explaining the mechanism is shown in Figure 3.5.

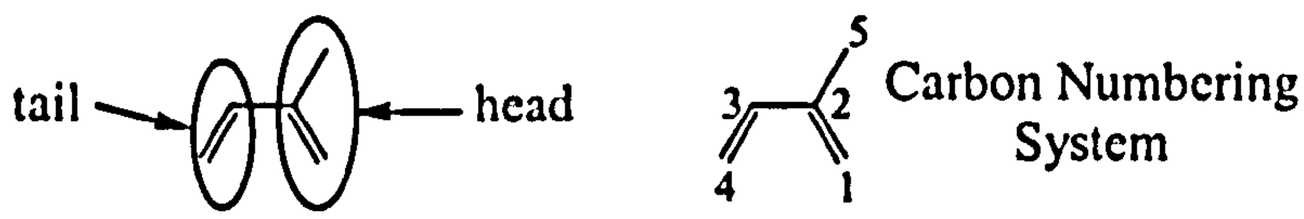
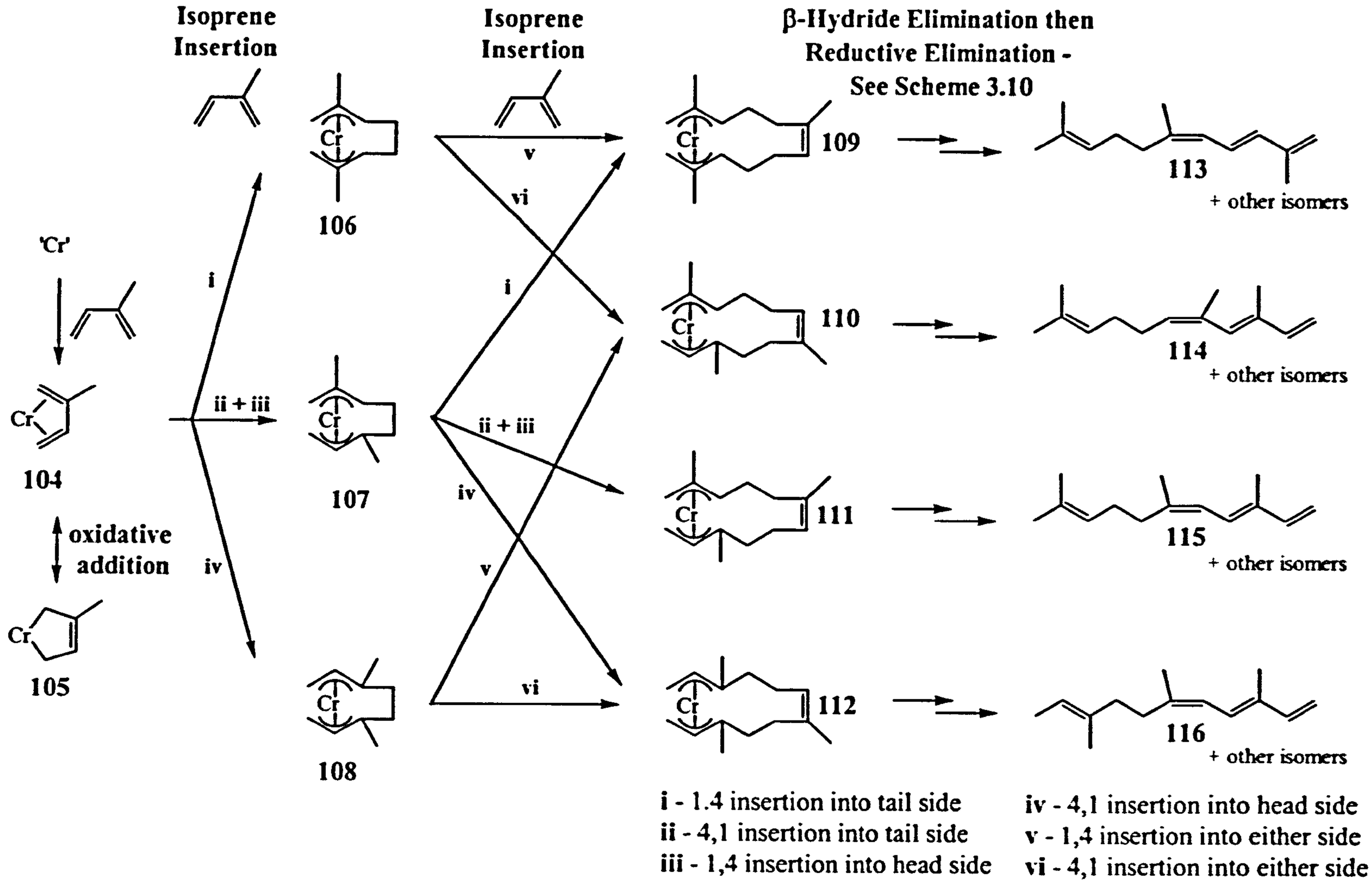
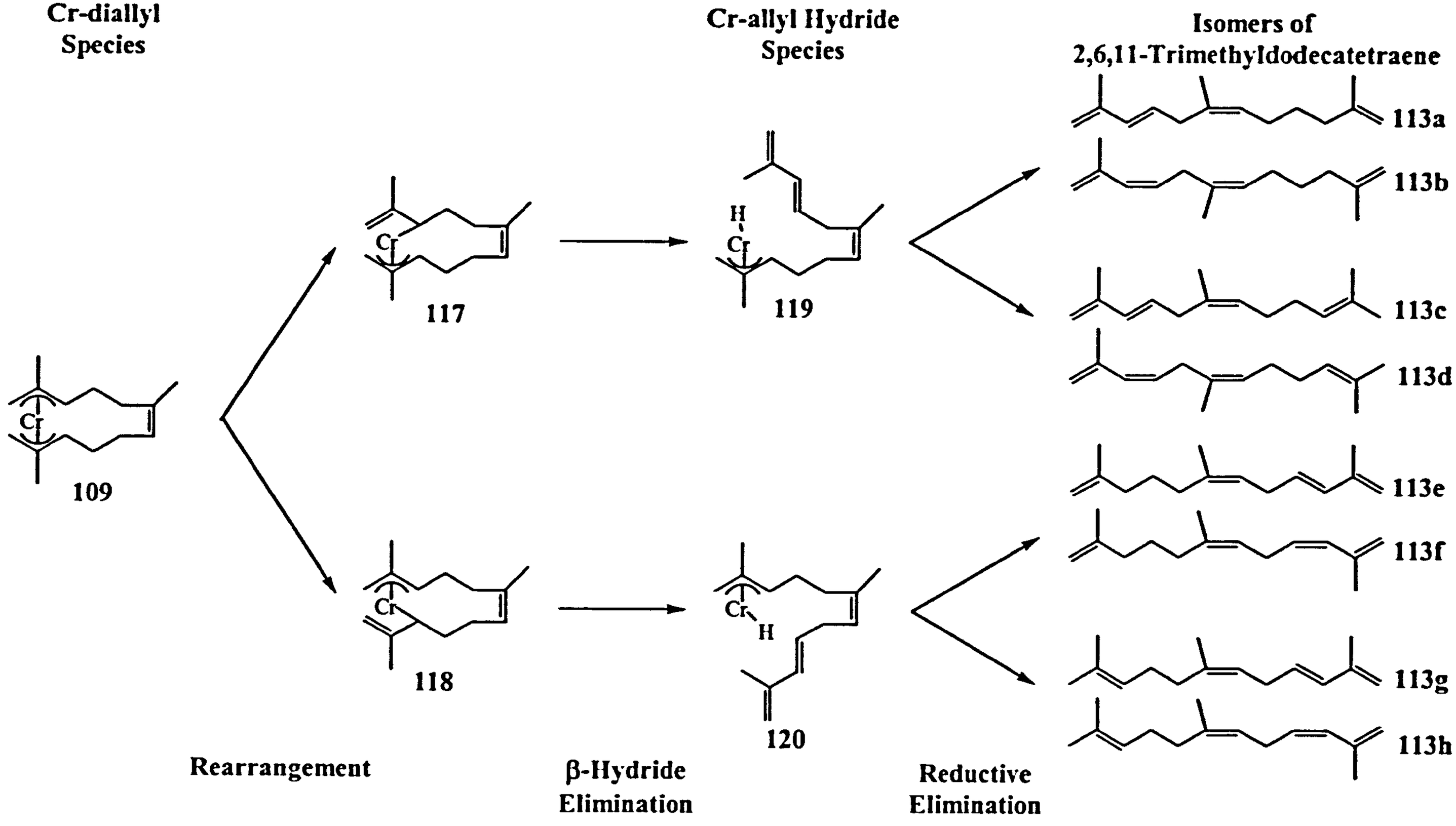


Figure 3.5 – Naming and Numbering System for Isoprene

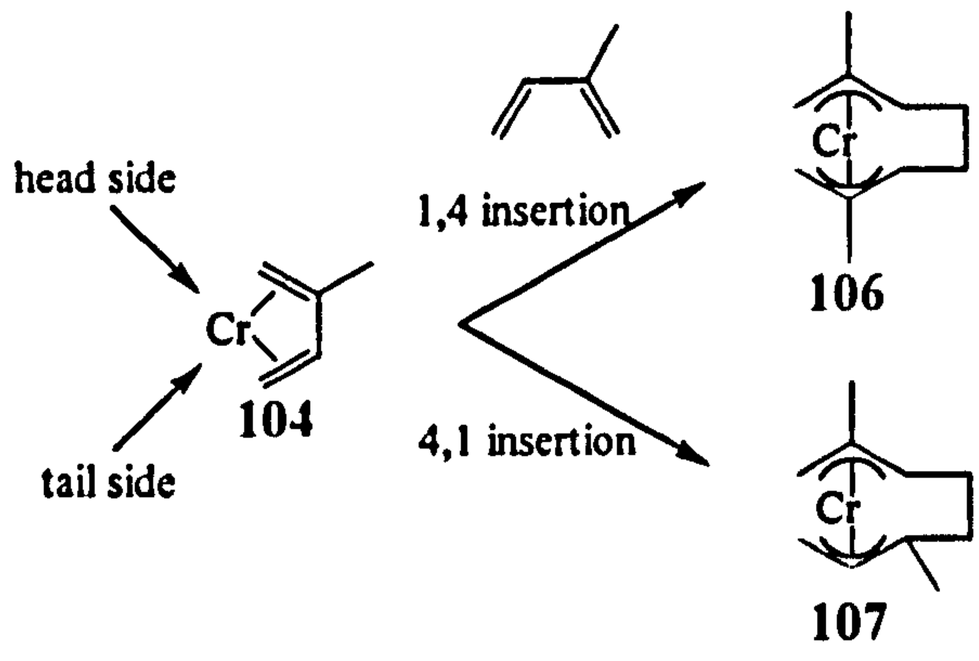


Scheme 3.9 – Mechanism for Trimerisation of Isoprene



Scheme 3.10 – Formation of Different Isomers of 2,6,11-Trimethyldodecatriene from Intermediate 109

In Scheme 3.9, the first isoprene coordinates to the Cr centre *via* 1,4 insertion to give **104**. Intermediate **104** can undergo oxidative addition to form metallacyclopentane **105**, which is similar to the metallacycle mechanism for ethene trimerisation. Next a second isoprene monomer inserts into intermediate **104**, to form the di-allyl chromium species **106**. Isoprene can insert two ways, depending on the position of the methyl group. Referring to the labelling Scheme in Figure 3.5, isoprene can insert *via* 1,4 insertion, where the methyl group is nearest the metal centre, or *via* 4,1 insertion where the methyl group is furthest away from the metal centre, as shown in Scheme 3.11.



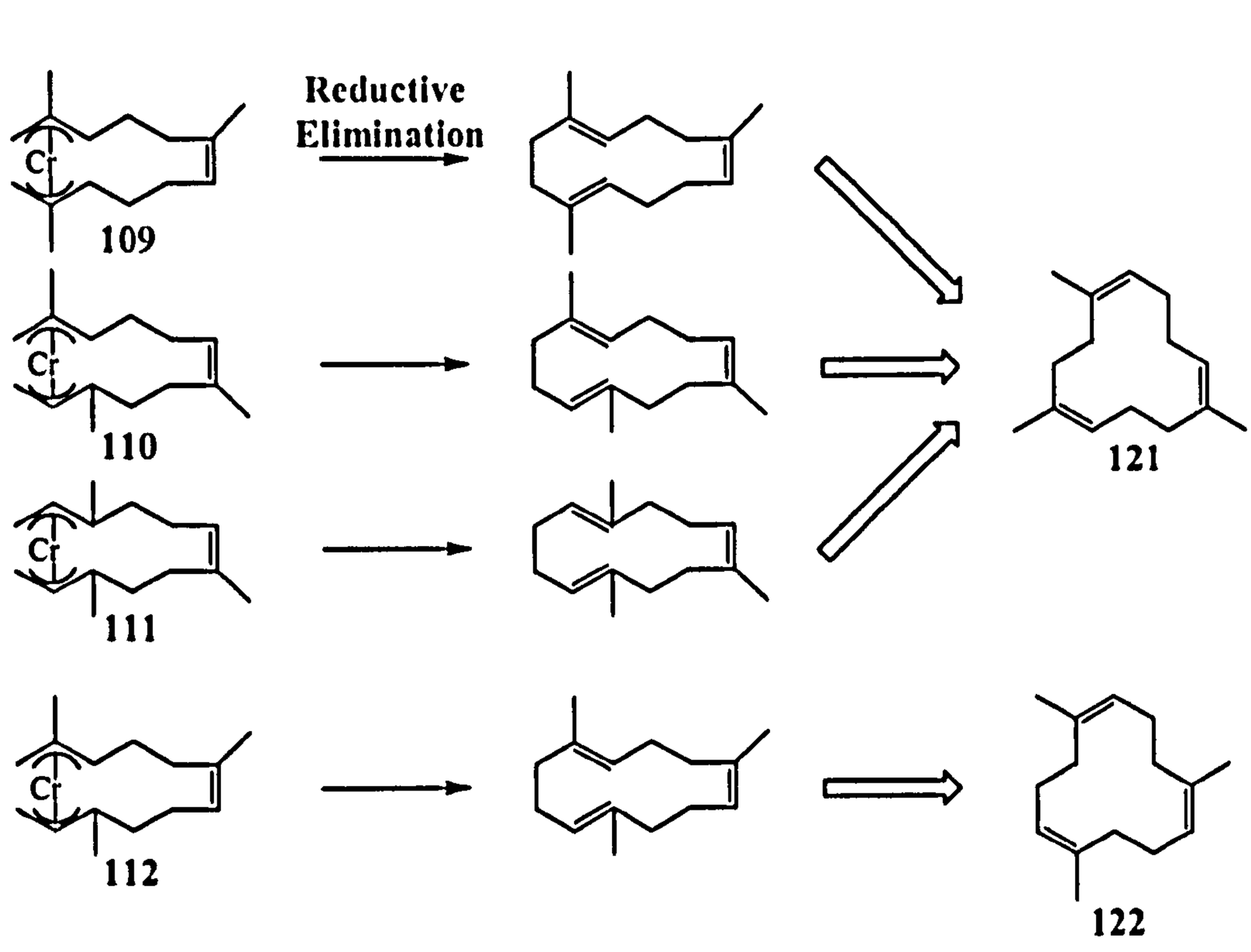
Scheme 3.11 – Isoprene Insertion into the Tail Side of Cr-allyl Species 104

The 1,4 insertion of isoprene is likely to be favoured because this forms the more stable 2-methyl-allyl group. Intermediate **104** is unsymmetrical due to the methyl group of isoprene, therefore insertion of isoprene either side of the metal forms different intermediates **106**, **107**, and **108**. This is denoted by assigning the side of isoprene with the methyl group as the 'head' and the side without the methyl group as the 'tail'. For example if isoprene inserts *via* a 1,4 insertion into the tail side of intermediate **104** then **106** is formed, if insertion occurs at the head side of **104** then **107** is formed.

The next step is the insertion of a third isoprene monomer into intermediates **106**, **107** and **108** to give **109 - 112**. As with the insertion of the second isoprene monomer, insertion of the third can occur *via* 1,4 or 4,1 insertion and either side of the metal centre, leading to four isomers of the seven-membered Cr-allyl intermediates, **109 - 112**. Intermediates **109 - 112** then undergo rearrangement, followed by β-hydride elimination and reductive elimination to give four structural linear isomers of isoprene trimers,

2,6,11-trimethyldodecatetraene, 113, 2,7,10-trimethyldodecatetraene, 114, 2,6,10-trimethyldodecatetraene, 115, 3,6,10-trimethyldodecatetraene, 116. An example of the rearrangement and reductive elimination of intermediates **109 - 112** is shown in Scheme 3.10. In the example shown intermediate **109** undergoes rearrangement either side of the Cr centre to give **117** or **112**, followed by β-hydride elimination to give Cr-allyl hydride species **119** and **120**. **119** and **120** can then undergo reductive elimination either at the 1- or 2-carbon position to give eight different isomers of **113** – **113a** to **113h**. The double bond in the 6 position is more likely to be a *cis* double bond, due to the constraints of the ring in intermediates **109** to **112** and so only one other double bond can have a *cis* or *trans* conformation giving the different isomers of **113**. Each of the intermediates **109** to **112** will undergo rearrangement, then β-hydride elimination and finally reductive elimination to give a total of 40 different isomers of **113**, **114**, **115** and **116** (See Appendix 8.2 for full isomer list of isomers).

Scheme 3.10 only shows the formation of linear trimers, cyclic trimers are also possible, as shown in Scheme 3.12.



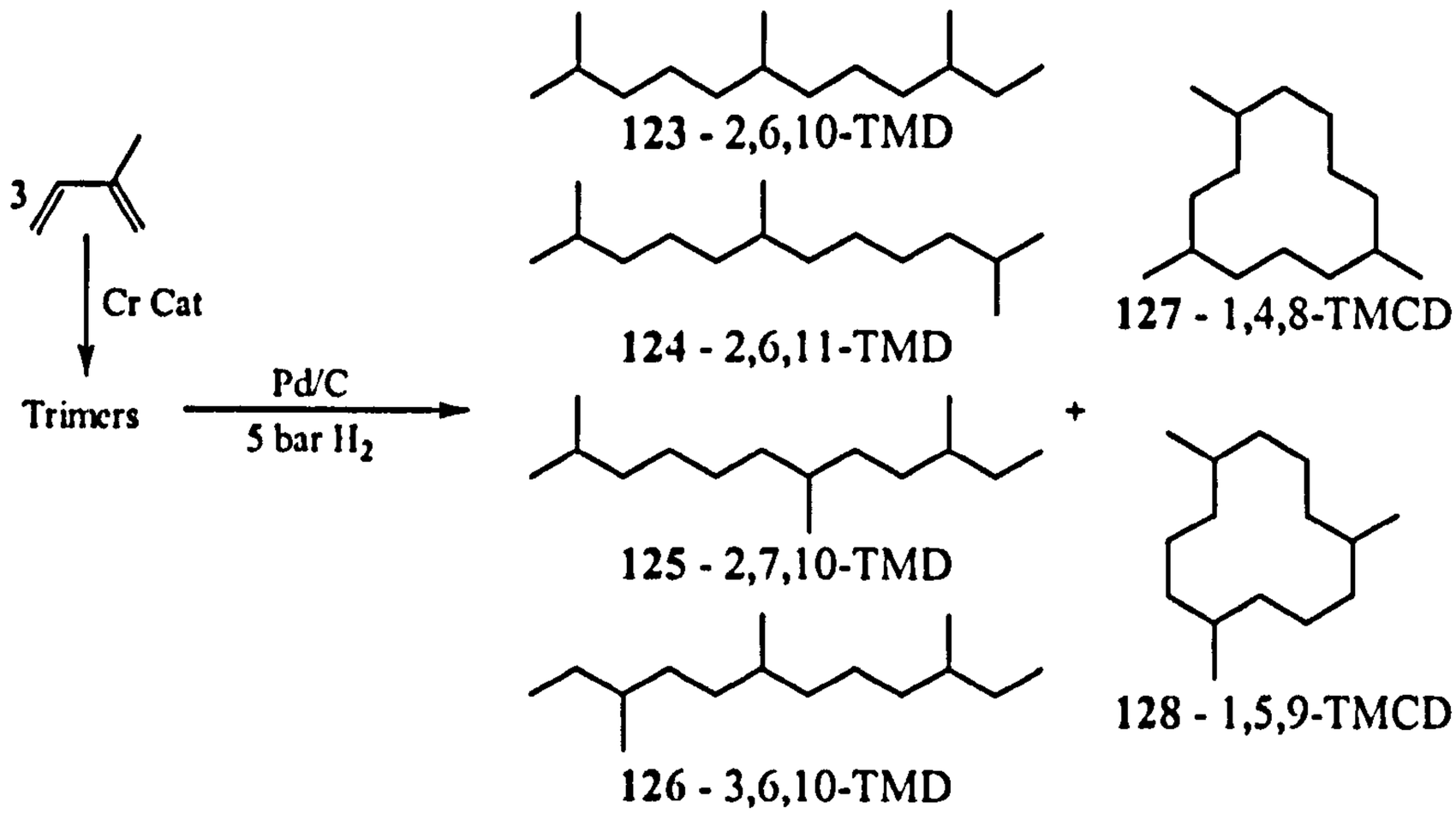
Scheme 3.12 – Formation of Isomers of Trimethylcyclododecatriene

Direct reductive elimination of intermediates **109**, **110**, **111** and **112** causes coupling of the two 'ends' of the chain to form cyclic trimers, giving 1,5,10-trimethyl-1,5,9-cyclododecatriene, **121**, and 1,5,9-trimethyl-1,5,9-cyclododecatriene, **122**.

Therefore overall there are four possible structural linear isomers and two possible cyclic isomers, depending on the position of the methyl groups. Although 42 different trimer isomers are possible if the position and stereochemistry of the double bond is taken into account.

3.3.2.2. Trimer Identification

The GC trace from an isoprene run, using the general conditions shown in Scheme 3.8, showed four trimer peaks and peaks for higher oligomers. As with the cotrimerisation of styrene and ethene (Chapter 2), in order to simplify the identification of the trimer products, hydrogenation of the trimer mixture was done in a autoclave, using palladium on carbon as the catalyst, under 5 bar of H_2, as shown in Scheme 3.13.[94] The possible isomers are 2,6,10-trimethyldodecane (2,6,10-TMD), **123**, 2,6,11-trimethyldodecane (2,6,11-TMD), **124**, 2,7,10-trimethyldodecane (2,7,10-TMD), **125**, 3,6,10-trimethyldodecane (3,6,10-TMD), **126**, 1,4,8-trimethylcyclododecane (1,4,8-TMD), **127** and 1,5,9-trimethylcyclododecane (1,5,9-TMD), **128** (Scheme 3.13).



Scheme 3.13 – Possible Hydrogenated Alkane Products from Isoprene Trimerisation

Upon hydrogenation, the GC trace of the trimer mixture showed that the four isoprene trimer peaks (unhydrogenated trimer products) had become two peaks (hydrogenated trimer products), corresponding to two different alkane products. The alkane trimers were then identified *via* comparison with the GC data and ^{13}C NMR spectroscopy of commercially available linear and cyclic standards 2,6,10-TMD, **123**, and 1,5,9-trimethyl-1,5,9-cyclododecatriene (a mixture of isomers), which was hydrogenated using Pd/C and H_2 to give 1,4,8-trimethylcyclododecane.[94] From this data it was deduced that the isomer with the lowest boiling point was a linear isomer and the other was a cyclic isomer. From the GC trace the product distribution of linear isomers to cyclic isomers was found for the $[CrCl_3(thf)_3]$/**1**/MAO system, this is shown in Table 3.4, the standard conditions shown in Scheme 3.8 were used.

Table 3.4 – Product Distribution of Hydrogenated Alkanes

Isomer	Product Distribution / %
Linear Isomer	55.2
Cyclic Isomer	23.9
Oligomers	20.9

From Table 3.4 it can been seen that the trimer mixture was made up of 55.2 % linear isomers, 23.9 % cyclic isomers and 20.9 % oligomers. The ^{13}C NMR data of the hydrogenated trimer mixture and the 2,6,10-trimethyldodecane standard are shown in Figures 3.6 and 3.7 respectively. The ^{13}C NMR spectrum of the 2,6,10-TMD, **123**, alkane standard was assigned using literature values (see Experimental, Chapter 6, for carbon numbering system).[132]

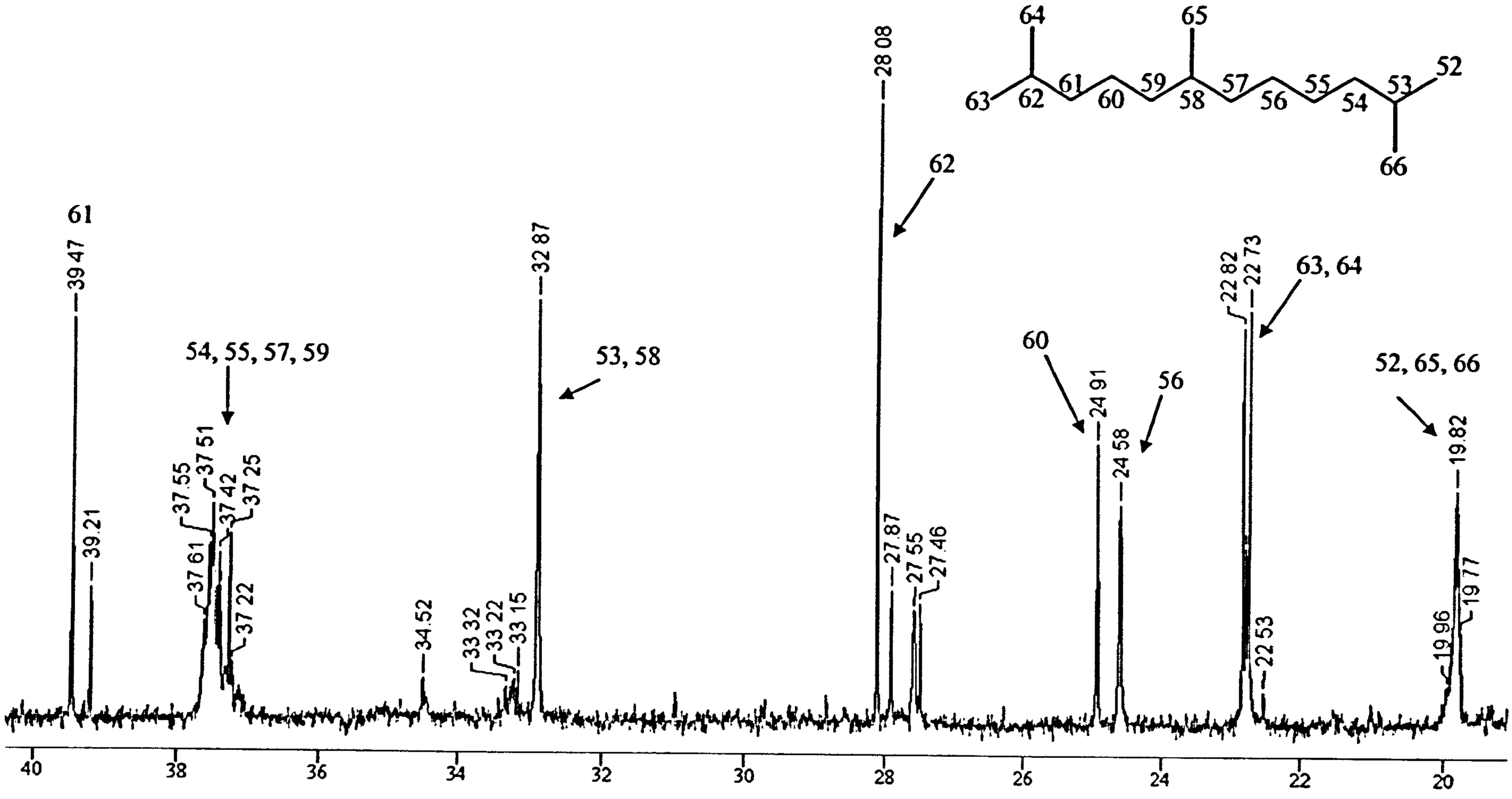


Figure 3.6 – ^{13}C NMR Spectrum of Hydrogenated Products from the Trimerisation of Isoprene

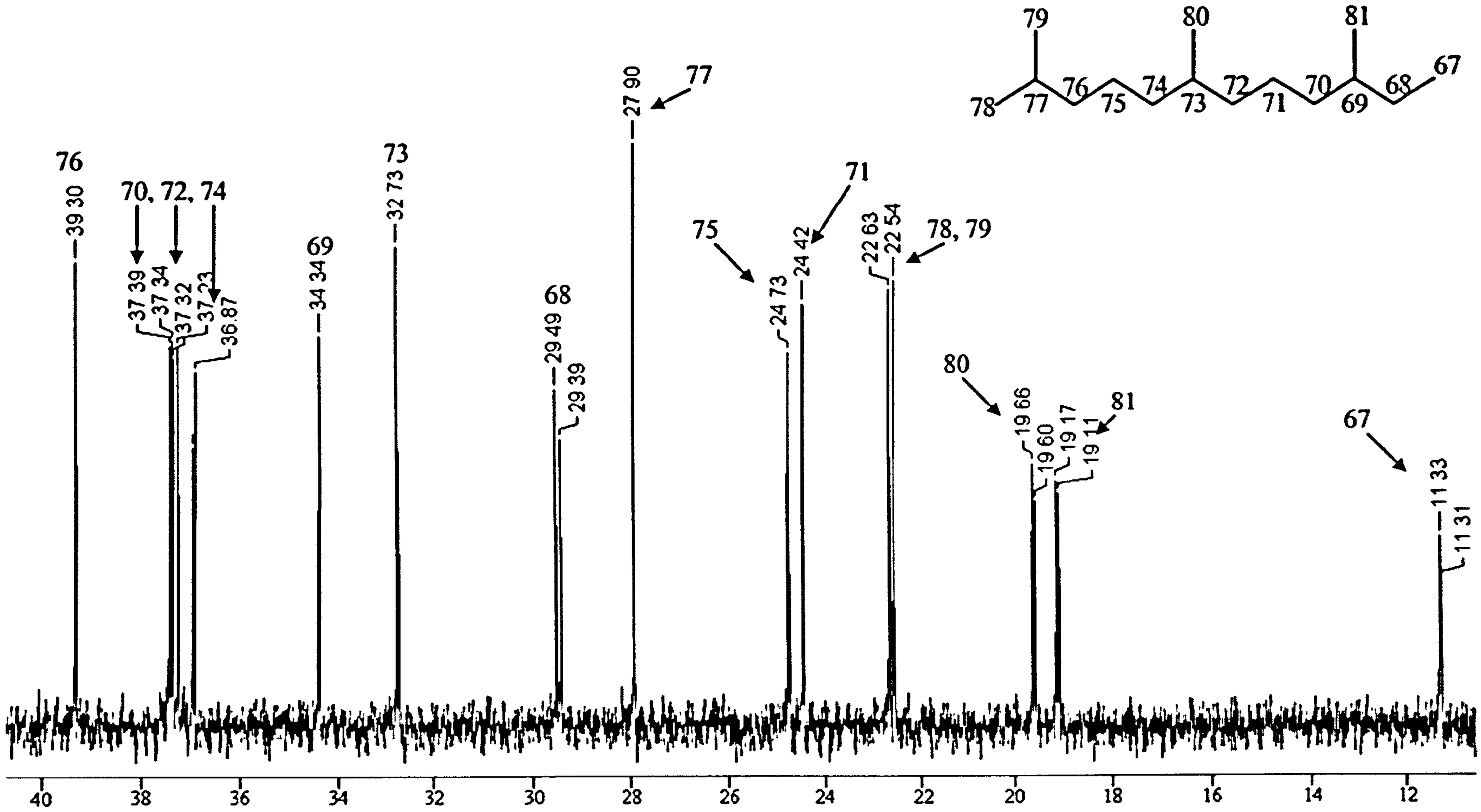
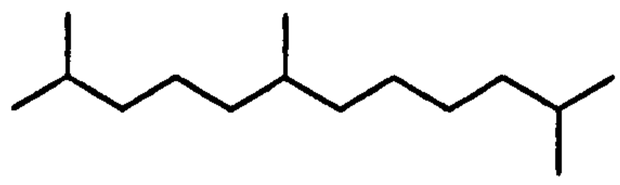


Figure 3.7 – ^{13}C NMR Spectrum of 2,6,10-Trimethyldodecane, 123, (Farnesane) Standard

The ^{13}C NMR spectrum of 2,6,10-TMD, **123**, in Figure 3.7 shows a peak at 11.32 ppm, corresponding to the terminal CH_3 group, C67, this is a characteristic peak for terminal CH_3 groups joined to a secondary CH_2 group. Linear isomers 2,6,10-TMD, **123**, 2,7,10-TMD, **125** and 3,7,10-TMD, **126**, all have this terminal CH_3 group and would therefore have a peak at about 11 ppm in the ^{13}C NMR spectrum. As can be seen in Figure 3.6 the ^{13}C NMR spectrum of the hydrogenated trimer mixture does not contain this peak, suggesting the linear alkane trimer peak is 2,6,11-TMD, **124**. Also other peaks on the spectrum of the alkane trimer (Figure 3.6) show similar shifts as that for carbons 70 to 80 from the 2,6,10-TMD, **123**, standard, suggesting that this end of the molecule is the same for both the standard and the linear trimer isomer. From this data it was deduced that the linear isomer in the hydrogenated trimer mixture is 2,6,11-TMD, **124**, as this is the only isomer without a terminal CH_3 group attached to a CH_2 group and carbons 55 to 65 have the same structure as carbon 70 to 80 of the standard, shown in Figure 3.8

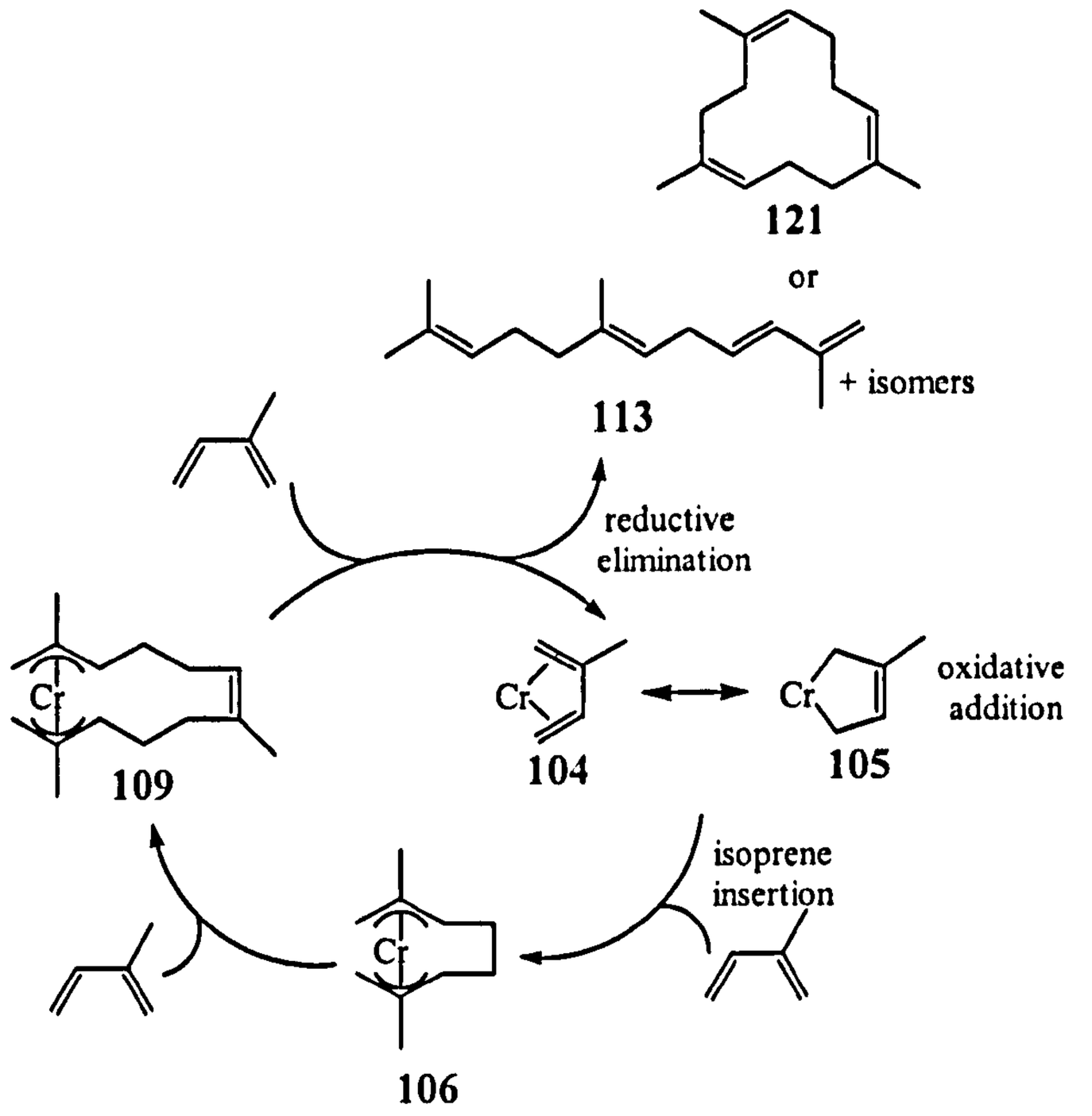
.



124- 2,6,11-trimethyldodecane
(2,6,11-TMD)

Figure 3.8 – Linear Isomer in Hydrogenated Trimer Mixture

The mechanism that forms the linear isomer 2,6,11-TMD is shown in Scheme 3.14.



Scheme 3.14 – Proposed Mechanism for Isoprene Trimerisation

The cycle goes *via* Cr-allyl intermediates **106** and **109**, which both have two 2-methyl-allyl groups, as shown in Figure 3.9. The 2-methyl-allyl group is more stable than the 3-methyl-allyl group because the methyl group stabilises the delocalisation of electrons within the group.

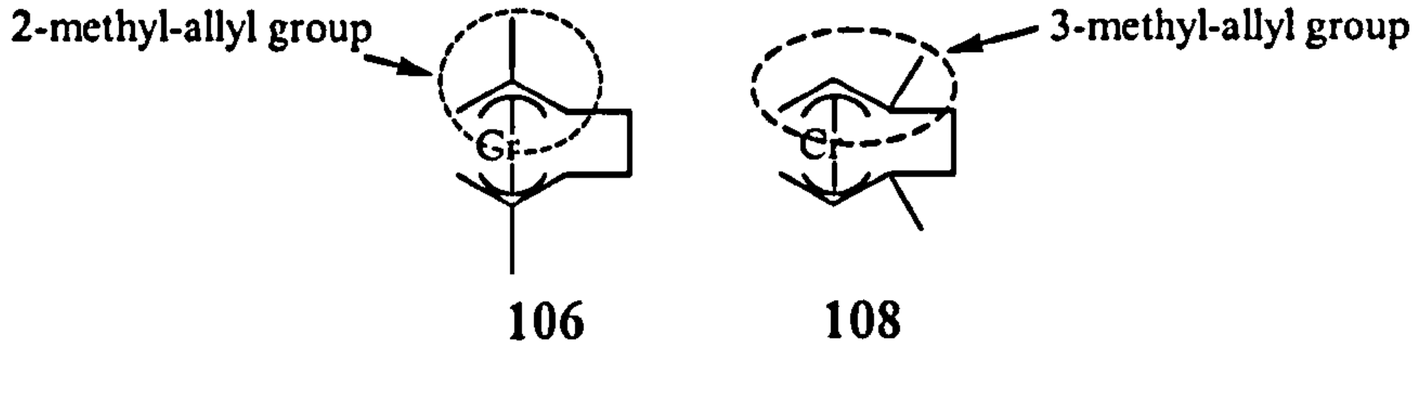


Figure 3.9 – Methyl-π-allyl Group in Intermediates 106 and 108

This formation of 2,6,11-trimethyldodecatetraene, **113** is consistent with the formation of intermediates with the 2-methyl-allyl groups, although it is not possible to deduce the exact position or stereochemistry of the double bonds in the linear isomer.

The structure of the cyclic isomer can be determined from this mechanism and from the comparison of the GC trace of the 1,5,9–trimethyl-1,5,9-dodecatriene (mixture of isomers) standard. It was deduced that the cyclic isomer is 1,5,10-trimethyl-1,5,9-cyclododecatriene, **121**. Therefore the trimer products from the trimerisation of isoprene using the $[CrCl_3(thf)_3]$/**1**/MAO system are shown in Figure 3.10.

2,6,11-trimethyldodecatetraene
113

1,5,10-trimethyl-1,5,9-cyclododecatriene
121

Figure 3.10 – Isoprene Trimers from $[CrCl_3(thf)_3]$/1/MAO system

It was then possible to determine which peaks on the GC for the isoprene trimer mixture corresponded to the linear and cyclic trimer isomers from the reaction mixture. It was found that there were three peaks for 2,6,11-trimethyldodecatetraene, **113**, and one peak for 1,5,10-trimethyl-1,5,9-cyclododecatriene, **121**.

From Scheme 3.10 it can be seen that eight isomers of 2,6,11-trimethyldodecatetraene, **113**, can be obtained (**113a** to **113h**). It is not possible to say which of these isomers is in the trimer mixture or which peak in the GC corresponds to which isomer; the GC peaks for two or more isomers may coincide. The product distribution of trimer isomers under standard conditions is shown in Table 3.5.

Table 3.5 – Product Distribution of Trimer Mixture from [$CrCl_3(thf)_3$]/1/MAO System

Trimers		Product Distribution / %
Linear Trimers **113**	C	12.7
	D	26.9
	E	15.6
Cyclic Trimer, **121**		23.9
Oligomers		20.9

Table 3.5 shows that the [$CrCl_3(thf)_3$]/**1**/MAO System give an overall selectivity of 12.7 % towards linear isomer **C** and 26.9 % and 15.6 % towards **D** and **E** respectively. An overall selectivity of 23.9 % towards the cyclic trimer was obtained and 20.9 % towards higher oligomers.

3.3.3. Effect of Changing Reaction Conditions on Products and Productivity

The aim of this section is to investigate how the productivity and selectivity of the products from the trimerisation of isoprene is affected by changing the conditions of the reaction. As stated in Section 3.1.1 the [$CrCl_3(thf)_3$]/**1**/MAO system (Scheme 3.7) was used and the standard conditions used were 0.02 mmol of [$CrCl_3(thf)_3$], 0.02 mmol of ligand **1**, 300 equivalents of MAO, 6.8 mol dm^{-3} of distilled isoprene and toluene was used as the solvent. The reaction was done at 70 °C and the reaction time was one hour.[93, 103, 128] The volume of each run was kept constant by changing the volume of toluene added compared to isoprene. The productivity was calculated from the mass of non-volatile products obtained from each run and the product distribution was calculated from GC data.

Table 3.6 shows the product distribution and selectivity from various catalytic runs where reaction conditions were changed. The distribution of linear and cyclic trimers is given as a percentage of the all the products.

Table 3.6 – Trimerisation of Isoprene Using Ligand 1

Run	Isoprene / mol dm^{-3}	Temper-ature / °C	Prod.[a]	TOF / h^{-1}	Product Distribution / wt %			
					Trimers			Oligo-mers
					Total	Linear Trimers[b]	Cyclic Trimers[b]	
3.4	0.5	70	73	56	82.0	26.6	55.4	18.0
3.5	2.3	70	510	390	86.9	53.2	33.7	13.1
3.6	4.5	70	530	405	68.8	52.9	15.9	31.2
3.7	6.8	70	826	632	79.1	55.2	23.9	20.9
3.8	6.8	57	400	306	74.7	56.2	18.5	25.3
3.9	6.8	45	349	267	68.2	60.0	8.2	31.8
3.10	6.8	25	19	15	100.0	72.9	27.1	0.0
3.11[c]	6.8	70	0	0	0	-	-	-
3.12[d]	6.8	70	0	0	0	-	-	-

[a] productivity / g (g Cr h)$^{-1}$; [b] overall selectivity; [c] no $[CrCl_3(thf)_3]$ added; [d] no MAO added.

Run 3.11 and 3.12 in Table 3.6 are control runs, where in run 3.11 no $[CrCl_3(thf)_3]$ was added and in run 3.12, no MAO was added, this was to show that the production of isoprene trimers was due to catalysis using $[CrCl_3(thf)_3]$, the PNP ligand and MAO and was not due to only MAO or $[CrCl_3(thf)_3]$. As can been seen there were no trimers present in either of these runs.

Run 3.4 to 3.7 show how the productivity of isoprene trimerisation changes with isoprene concentration, these results are shown graphically in Figure 3.11.

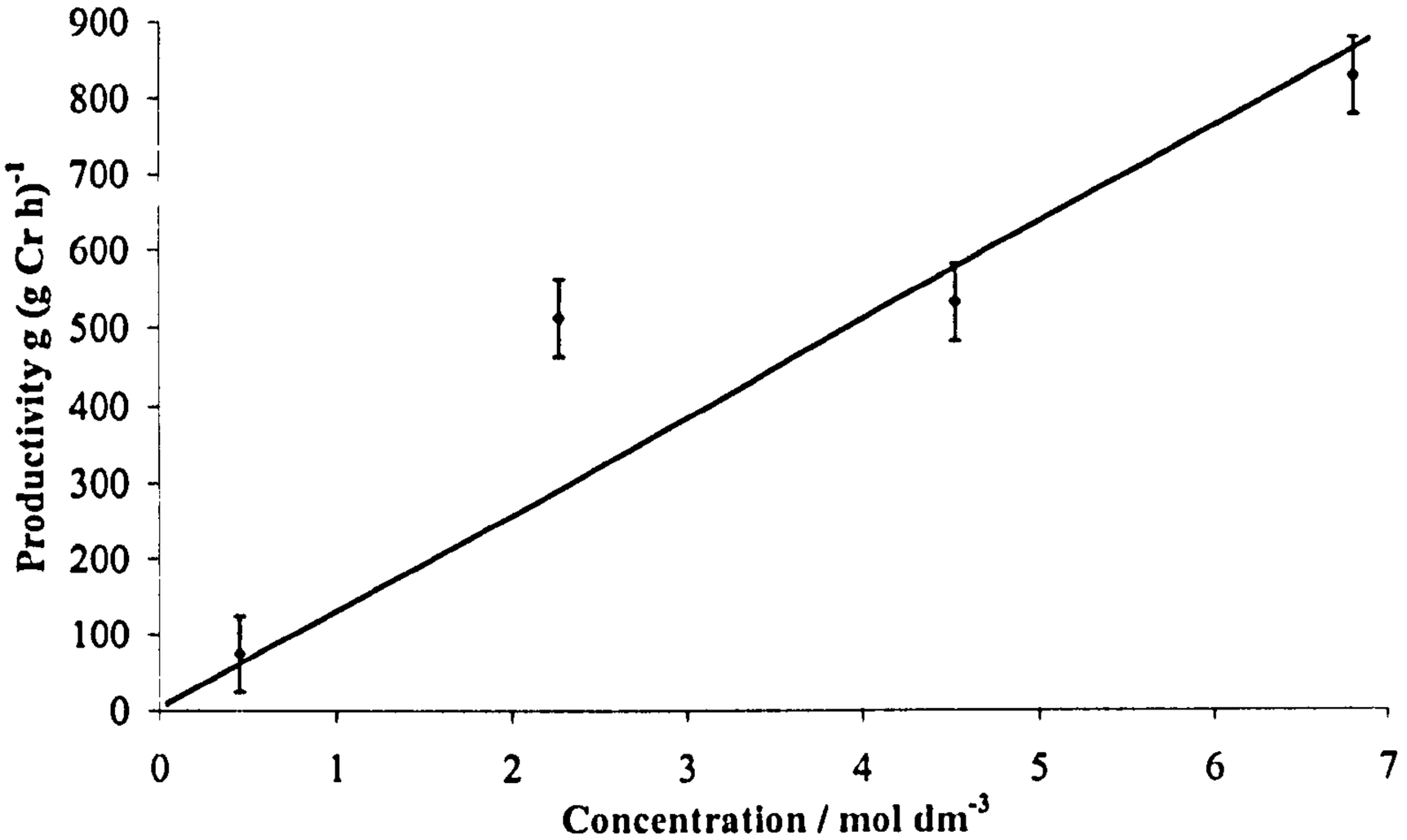


Figure 3.11 – Change in Productivity with Isoprene Concentration

The graph in Figure 3.11 shows that productivity increases linearly with isoprene concentration. This is because increasing the isoprene concentration causes the rate of the reaction to increase. There are many methods in which the catalyst may be deactivated; one method is that at a high concentration of isoprene other Cr-allyl complexes may be formed, where isoprene irreversibly binds to the metal centre. Another method may be that there is a small concentration of a catalyst poison in isoprene which increases in concentration along with isoprene. Figure 3.10 implies that the effect of catalyst deactivation is small in this system because there is no evidence of a reduction in rate of increase in productivity. Also Figure 3.11 suggests that the productivity is first order in relation to isoprene concentration.

Figure 3.12 shows how the product distribution changes with isoprene concentration.

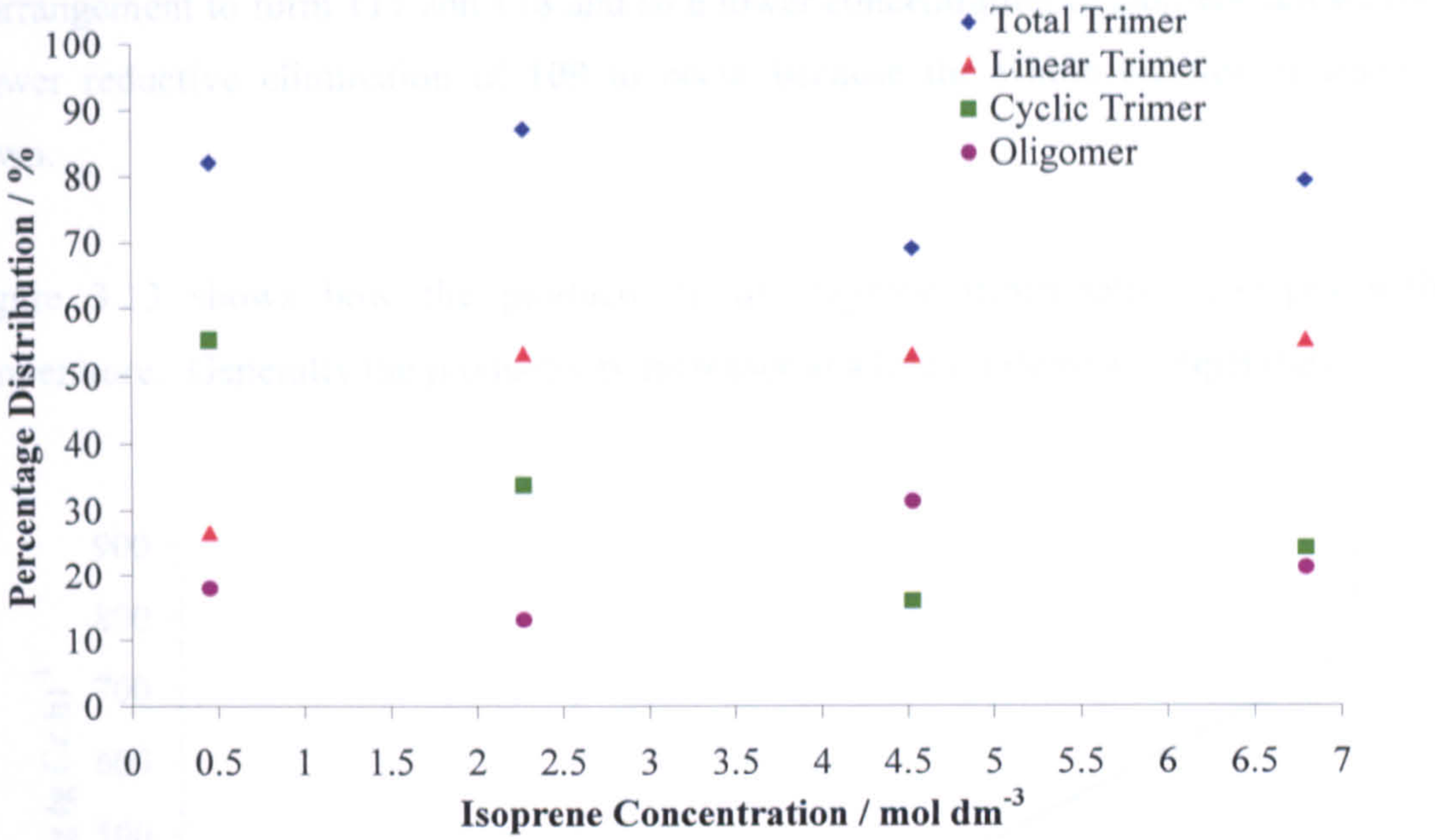


Figure 3.12 – Change in Product Distribution with Isoprene Concentration

From Figure 3.12 is can be seen that the overall product distribution of the linear and cyclic trimers is shown. It can be seen that generally as the concentration of isoprene is increased the total percentage of trimer deceases and the percentage of oligomers present increases. The formation of trimers is due to the rate of reductive elimination (cyclic isomer) or rearrangement (linear isomers) of intermediate **109** (see Section 3.3.2.1) being higher than the insertion of another isoprene unit. If the concentration of isoprene is increased then the probability of the insertion of isoprene into the catalytic cycle becomes higher and therefore increasing the percentage of oligomers in the reaction mixture. Also if there is any incorporation of trimers back into the catalytic cycle, the increase in productivity with concentration would cause the likelihood of this happening to increase and in turn increase the percentage of oligomers produced.

The ratio of linear trimers to cyclic trimers increases with isoprene concentration, where as the percentage of linear isomers increases and the percentage of the cyclic isomer decreases. The formation of the linear isomers over the cyclic isomer depends on the rate of reductive elimination of intermediate **109** to give the cyclic isomer (Scheme 3.12), compared to that of the rearrangement to form intermediates **117** and **118** (Scheme 3.10). This suggests that the reductive elimination of **109** is slower than the

rearrangement to form **117** and **118** and so a lower concentration of isoprene allows the slower reductive elimination of **109** to occur because the whole reaction is slowed down.

Figure 3.13 shows how the productivity of isoprene trimerisation changes with temperature. Generally the productivity increases at a linear rate with temperature.

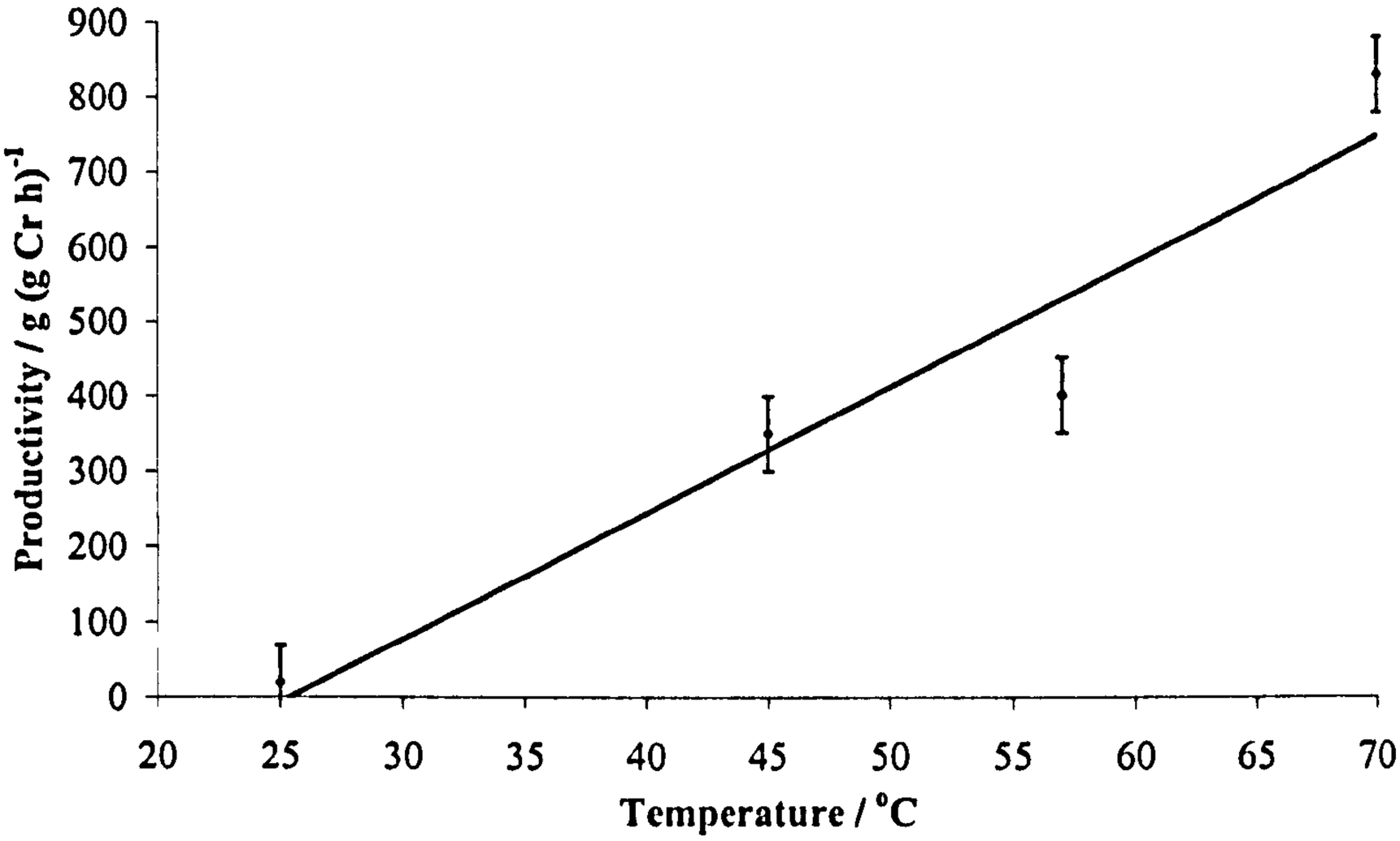


Figure 3.13 – Change in Productivity with Temperature

At 25 °C only a small productivity of 19 g (g Cr h)$^{-1}$ is seen, whereas at 70 °C a productivity of 826 g (g Cr h)$^{-1}$ is seen. Unlike ethene trimerisation, where for the $[CrCl_3(thf)_3]$/1/MAO system a productivity of 8900 g (g Cr h)$^{-1}$ is obtained at 25 °C, a higher temperature is needed for isoprene trimerisation to occur. This may be because the allyl intermediates formed in the mechanism (see Section 3.3.1.2) may be more stable than the metallacyclopentane or metallacycloheptane intermediates formed in mechanism of ethene trimerisation (see Section 1.5.1).

Figure 3.14 shows the change in product distribution with respect to reaction temperature.

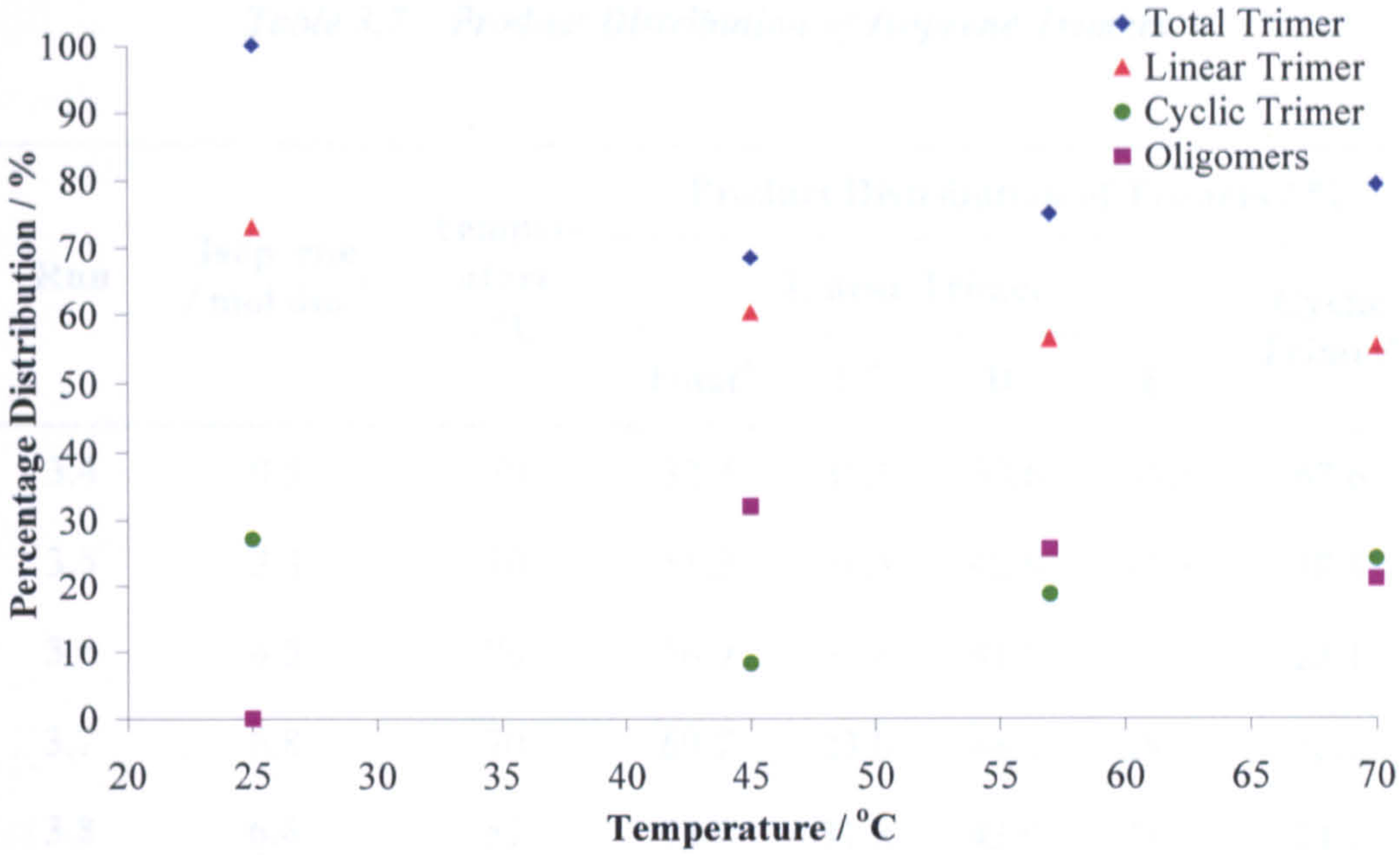


Figure 3.14 – Change in Product Distribution with Reaction Temperature

As with increasing the concentration, increasing the temperature increases the percentage of oligomers and decreases the total trimer fraction. Generally the ratio of linear to cyclic trimers decreases with temperature, where the percentage of linear trimers decreases and the percentage of cyclic trimer increases, which is the opposite to what happens when isoprene concentration is increased. This suggests that increasing the temperature increases the rate of reductive elimination of intermediate **109** (Scheme 3.12) more than the rate of rearrangement to **117** and **118** (Scheme 3.10), thus increasing the percentage of cyclic trimers compared to linear trimers.

Table 3.7 shows the product distribution of linear and cyclic trimers within the trimer fraction. The table shows linear trimers **C**, **D** and **E**, this refers to the three peaks on the GC trace and not specific trimers. This is because it is not known exactly how many trimer isomers are produced; as the peaks of two different isomers may coincide on the GC trace and appear as one. The percentage selectivities given for **C**, **D** and **E** are within the linear trimer fraction.

Table 3.7 – Product Distribution of Isoprene Trimers

Run	Isoprene / mol dm^{-3}	Temper-ature / °C	Product Distribution of Trimers / %				
			Linear Trimers				Cyclic Trimer[a]
			Total[a]	C[b]	D[b]	E[b]	
3.4	0.5	70	32.4	36.1	30.6	33.3	67.6
3.5	2.3	70	61.2	31.3	42.9	25.8	38.8
3.6	4.5	70	76.9	32.8	41.9	25.3	23.1
3.7	6.8	70	69.7	23.0	48.7	28.3	30.2
3.8	6.8	57	75.2	31.8	43.9	24.3	24.8
3.9	6.8	45	87.9	37.2	42.8	20.0	12.1
3.10	6.8	25	72.9	20.5	46.7	32.8	27.1

[a] within trimer fraction; [b] within linear trimer fraction.

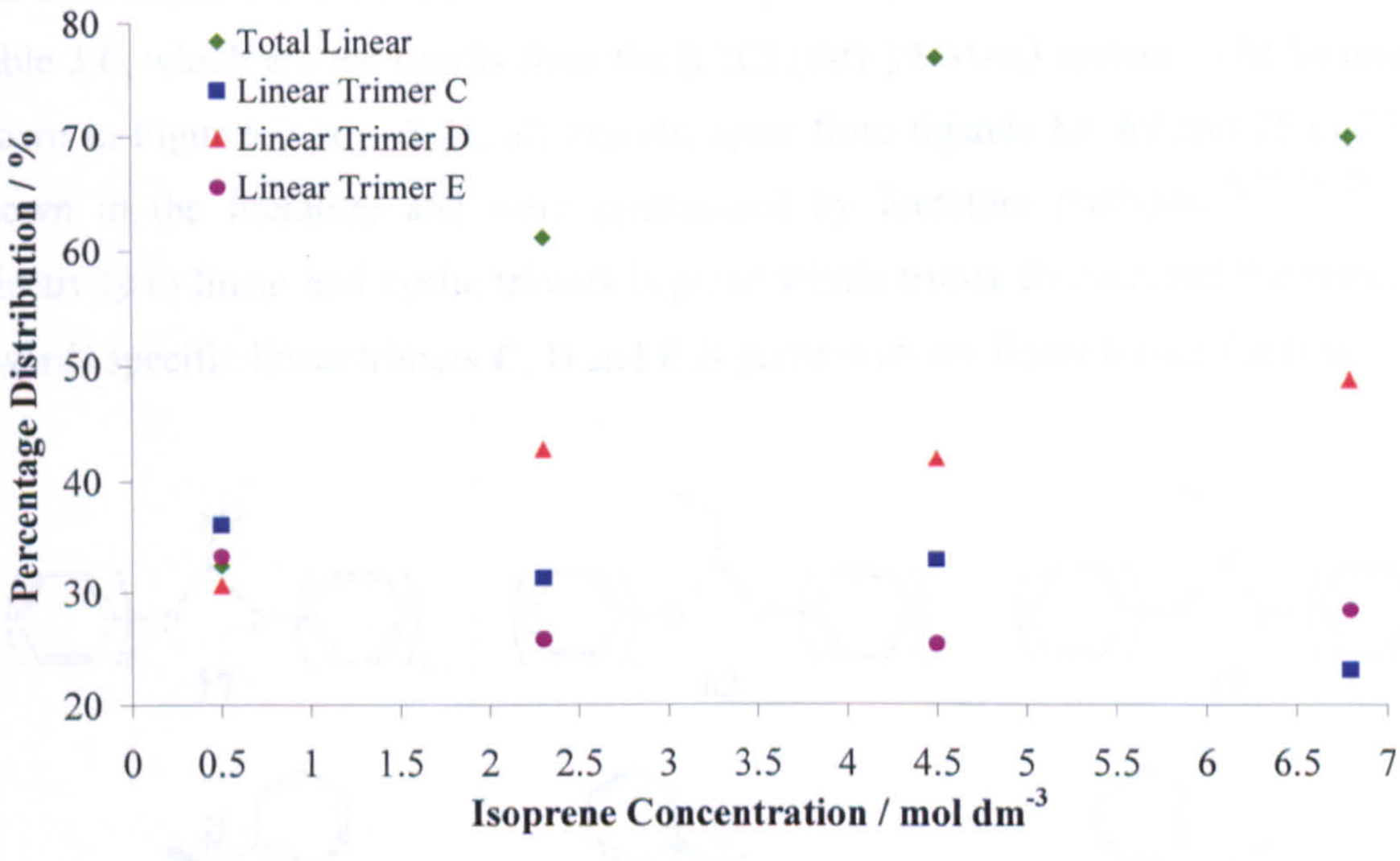


Figure 3.15 – Change in Distribution within Linear Trimer Fraction with Isoprene Concentration

Figure 3.15 shows how the product distribution within the trimer fraction changes with isoprene concentration. As the concentration of isoprene is increased the percentage of linear trimers **C** and **E** decrease, whereas the percentage of **D** increases. It is not possible to state why this occurs because the linear trimer labels refer to the three linear trimer peaks on the GC trace and not to a specific isomers of 2,6,11-trimethyldodecatetraene.

3.3.4. Trimerisation of Isoprene with Systems Using Other PNP Ligands

A variety of PNP, bis(diarylphosphino)ethane and bis(diarylphosphino)methane ligands were synthesised and tested. The conditions used were 0.04 mmol of $[CrCl_3(thf)_3]$, 0.04 mmol of ligand, 300 equivalents of MAO co-catalyst, a temperature of 70 °C and a reaction time of for 1 hour. The concentration of isoprene used was 6.8 mol dm^{-3} and toluene was used as the solvent, with a total volume of 44 mL for each run. The results obtained are shown in Tables 3.8 to 3.12, the productivity in each table was determined from the mass gain of non-volatile products from each run and the product distribution was determined from the GC data. For a comparison, each table contains run 3.7 from Table 3.6, which are the results from the $[CrCl_3(thf)_3]$/**1**/MAO system. The ligands are shown in Figures 3.16 – 3.21, all ligands, apart from ligands **68**, **69** and **75** to **77**, are known in the literature and were synthesised by literature methods.[36, 37, 41, 42] The selectivity to linear and cyclic trimers is given within trimer fraction and the selectivity towards specific linear trimers **C**, **D** and **E** is given with the linear trimer fraction.

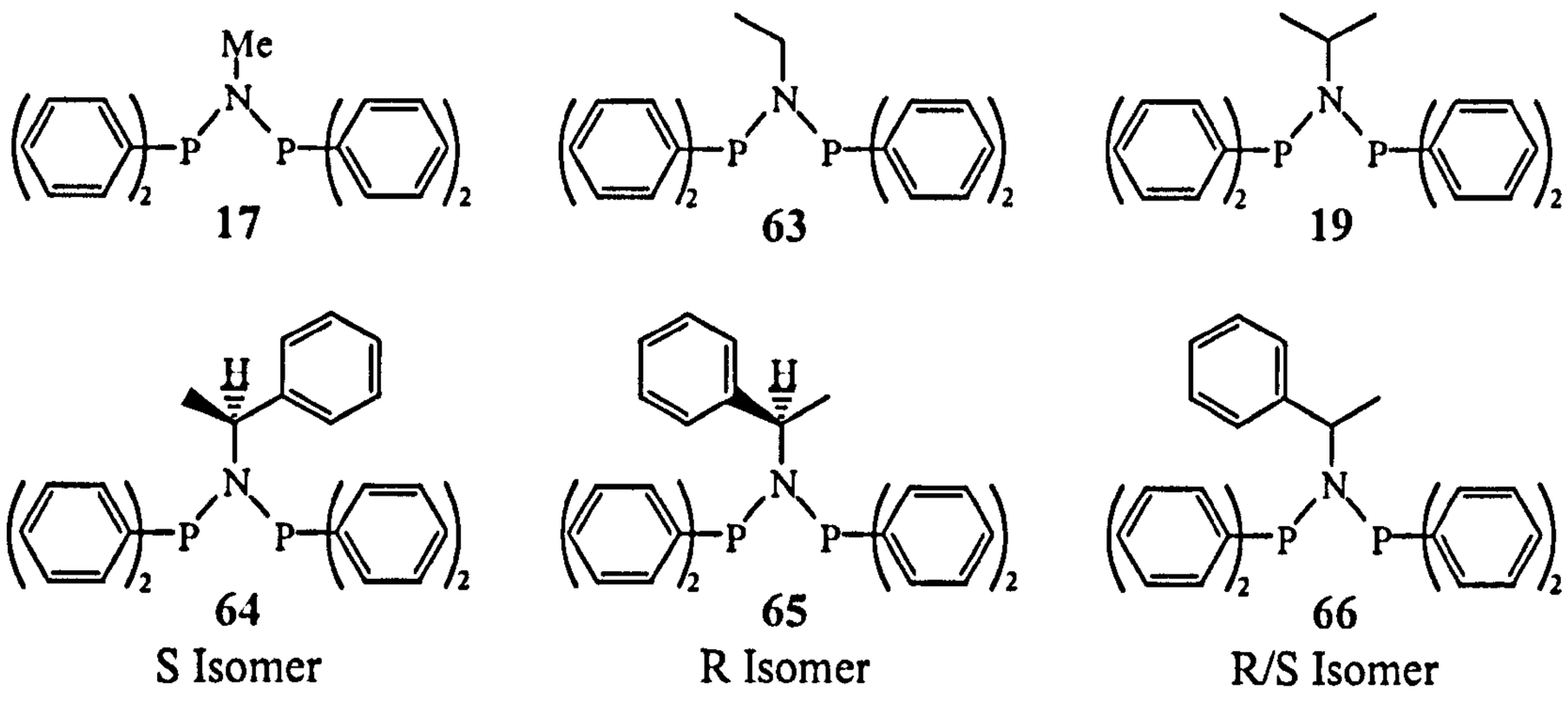


Figure 3.16 – PNP Ligands with Alkyl Substituents on Nitrogen

Table 3.8 – Isoprene Trimerisation with Ligands in Figure 3.15

Run	Ligand	Prod.[a]	TOF / h^{-1}	Product Distribution (wt %)						
				Trimers						C_{20+}[b]
				Total[b]	Linear Trimers				Cyclic[c]	
					Total[c]	C[d]	D[d]	E[d]		
3.7	**1**	826	632	79.1	70.0	33.2	48.9	17.9	30.0	20.9
3.13	**17**	370	283	6.6	76.1	28.5	41.3	30.2	23.9	93.4
3.14	**63**	315	241	13.1	73.4	32.3	43.7	24.0	26.6	86.9
3.15	**19**	298	228	28.7	49.8	27.3	37.8	35.7	50.1	71.3
3.16	**64**	375	287							
3.17	**65**	577	441	No Trimer – 100 % oligomers to polymer						
3.18	**66**	423	323							

[a] Productivity / g (g Cr h)$^{-1}$; [b] overall selectivity; [c] within trimer fraction; [d] within linear trimer fraction;

Table 3.8 shows how the substituent on the nitrogen backbone affects the productivity and product distribution. As the size and bulk of the substituent on the nitrogen is increased, the selectivity towards trimer products decreases. This suggests that having bulky substituents on the nitrogen, changes the selectivity of the reaction from isoprene trimerisation to isoprene oligomerisation or polymerisation. This is consistent with the insertion of isoprene being faster than the rearrangement or reductive elimination, in systems using PNP ligands with bulky nitrogen substituents. This is seen with ethene trimerisation, where increasing the bulk of the nitrogen substituent increases the selectivity to octene over hexene, although it is unclear as to why this occurs.[41, 48] Generally as the size of the nitrogen substituent increases the productivity decreases with 370 g (g Cr h)$^{-1}$ for ligand **17**, with a methyl group on the nitrogen and 298 g (g Cr h)$^{-1}$ for ligand **19**, with an isopropyl group on the nitrogen. The percentage of cyclic to linear trimer is highest for run 3.15, ligand **19**, suggesting that the reductive elimination of intermediate **109** is favoured over the rearrangement to **117** and **118** for ligands with bulky groups on the nitrogen.

The productivity for ligand **17** is 370 g (g Cr h)$^{-1}$ compared to 826 g (g Cr h)$^{-1}$ for ligand **1**, showing that the OMe groups on ligand **1** plays a large part in catalysis. This lead to the testing of a range of PNP ligands with *ortho* alkyl groups on the phenyl ring, as shown in Figure 3.17 and the results are shown in Table 3.9.

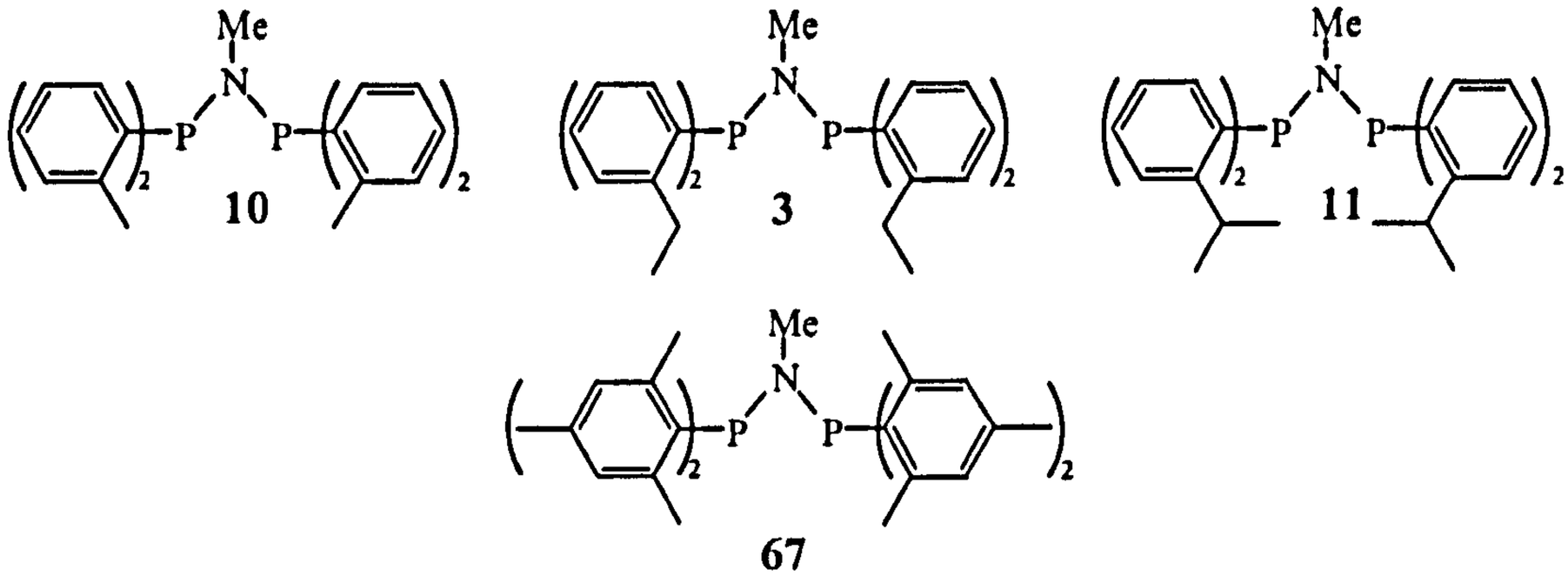


Figure 3.17 – PNP Ligands with Alkyl Substituents

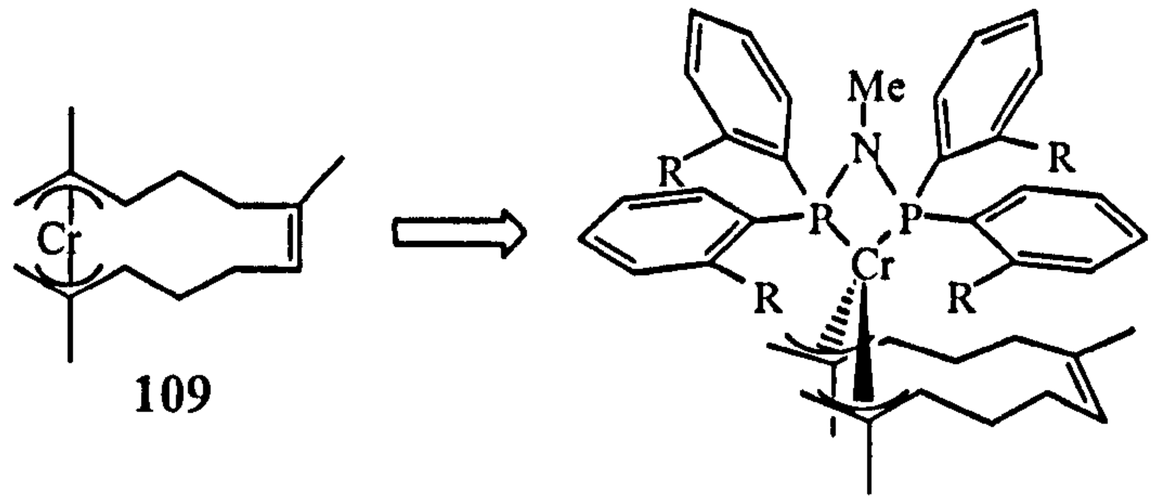
Table 3.9 – Isoprene Trimerisation with Ligands in Figure 3.16

Run	Ligand	Prod.[a]	TOF / h^{-1}	Product Distribution (wt %)						
				Trimers						C_{20+}[b]
				Total[b]	Linear Trimers				Cyclic[b]	
					Total[c]	C[d]	D[d]	E[d]		
3.7	**1**	826	632	79.1	70.0	33.2	48.9	17.9	30.0	20.9
3.19	**10**	663	507	94.9	74.2	27.0	44.3	28.7	25.8	5.1
3.20	**3**	701	536	71.2	78.3	25.3	45.0	29.7	21.7	29.8
3.21	**11**	697	533	59.6	79.5	26.3	46.5	27.2	20.5	40.4
3.22	**67**	769	588	66.5	76.3	19.6	33.3	23.5	23.7	33.5

[a] Productivity / g (g Cr h)$^{-1}$; [b] overall selectivity; [c] within trimer fraction; [d] within linear trimer fraction;

It was found that bulky *ortho* groups on the phenyl rings of the PNP ligands give higher productivity and higher selectivity to trimeric products than PNP ligands without the *ortho* groups. This may be because the bulky *ortho* groups cause the rate of

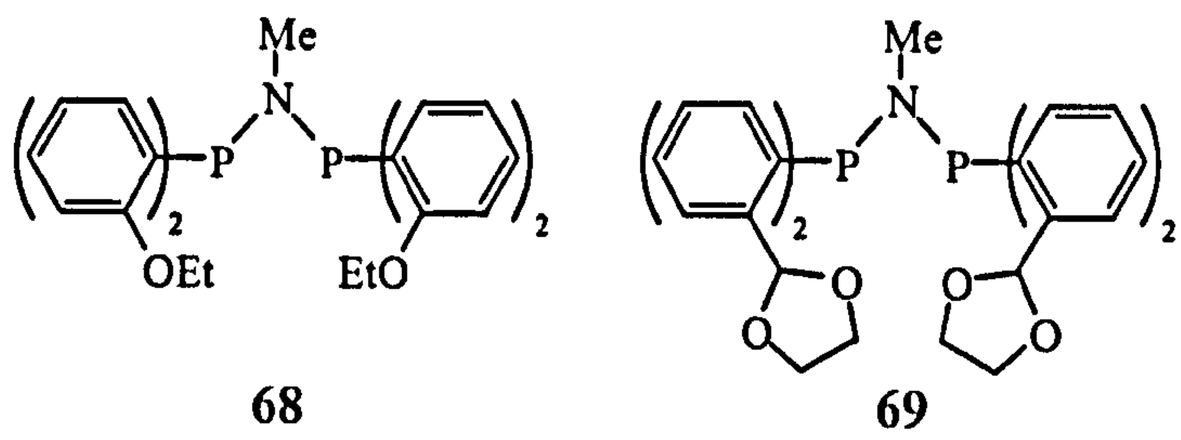
rearrangement of diallyl intermediate **109** to **117** and **118** to increase and become favoured over insertion of further isoprene units. Ligand **67** showed the most promising results, out of this group of ligands, with a productivity of 769 g (g Cr h)$^{-1}$, this ligand has methyl groups on the *ortho* positions in each aryl group so is more sterically hindered than PNP ligands with one *ortho* group on each aryl ring. Figure 3.18 shows how the PNP ligand may be positioned in intermediate **109**.



109

Figure 3.18 – Interaction Between Ligand and Intermediate 109

It may be expected that as the size of the R group is increased from Me to *i*Pr then the selectivity towards the trimer product would increase because further isoprene insertion would become more difficult. Table 3.9 shows that this is not the case, the selectivity towards the trimer product is 94.9 % for ligand **10**, whereas the selectivity is 59.6 % for ligand **11** where R is *i*Pr. The product distribution within the trimer fraction stays constant, although compared to run 3.7, the percentage of linear trimer is slightly higher. Run 3.7, with ligand **1** still shows a higher productivity than this group of ligands, which then leads on to the testing of other PNP ligands with oxygen donor substituents in the *ortho* position on the aryl rings, as shown in Figure 3.19.



68 **69**

Figure 3.19 – PNP Ligands with Oxygen Based Substituents

Table 3.10 – Isoprene Trimerisation with Ligands in Figure 3.18

Run	Ligand	Prod.[a]	TOF / h^{-1}	Product Distribution (wt %)						
				Trimers						C_{20+}[b]
				Total[b]	Linear Trimers				Cyclic[b]	
					Total[c]	C[d]	D[d]	E[d]		
3.7	**1**	826	632	79.1	70.0	33.2	48.9	17.9	30.0	20.9
3.23	**68**	576	440	89.7	68.9	27.5	47.3	25.2	20.8	10.3
3.24	**69**	1,370	1,048	79.0	60.8	31.9	48.5	19.6	18.2	21.0

[a] Productivity / g (g Cr h)$^{-1}$; [b] overall selectivity; [c] within trimer fraction; [d] within linear trimer fraction;

Table 3.10 shows the results obtained from the systems using PNP ligands with oxygen donor substituents in the *ortho* position on the aryl rings. Compared to **1**, ligand **68** with ethoxy groups on the aryl ring gave a lower productivity of 576 g (g Cr h)$^{-1}$, although the trimer selectivity was higher at 89.7 %. Ligand **69** gave a productivity of 1,370 g (g Cr h)$^{-1}$, this may be because the acetal groups on the aryl rings are bulky and so as previously stated from the PNP ligand in Figure 3.17, the bulkier the substituent in the *ortho* position of the aryl groups, the higher the productivity towards isoprene trimerisation. The selectivity towards the trimeric products for **69** is 79.0 %, with a selectivity of 60.8 % to linear trimers within the trimer fraction.

A range of bis(phenylphosphino)ethane, dppe, derivatives were also tested for isoprene trimerisation, shown in Figure 3.20. Ligand **71**, dppe, has previously been shown to have a low activity for ethene trimerisation.[47]

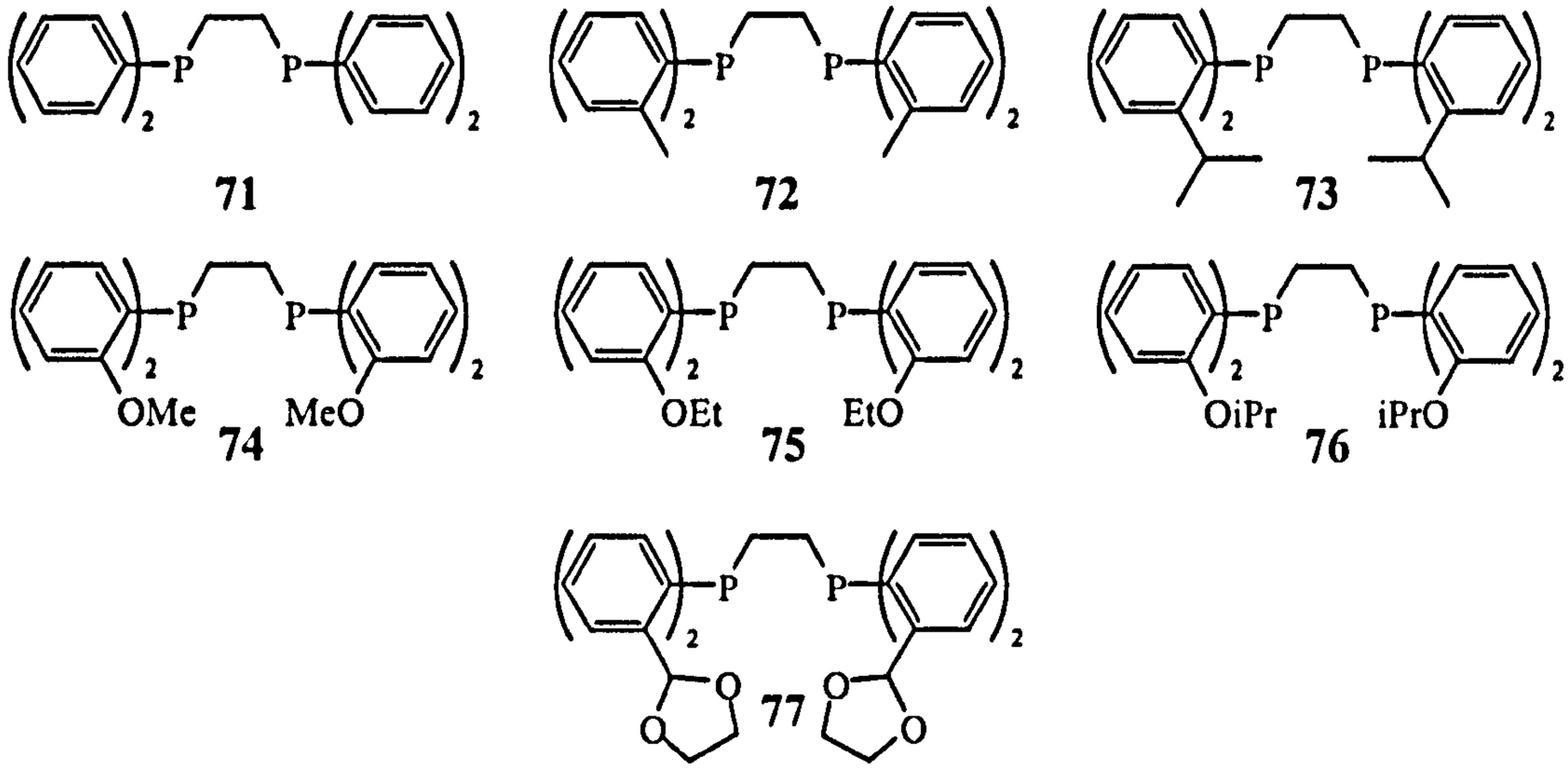


Figure 3.20 – Bis(diarylphosphino)ethane Ligands Tested for Isoprene Trimerisation

Ligands based on dppe were found to be inactive towards isoprene trimerisation. Other than dppe, these ligands were found to be inactive for ethene trimerisation or tetramerisation and in Chapter 2, these ligands were also inactive towards ethene and styrene cotrimerisation.[4]

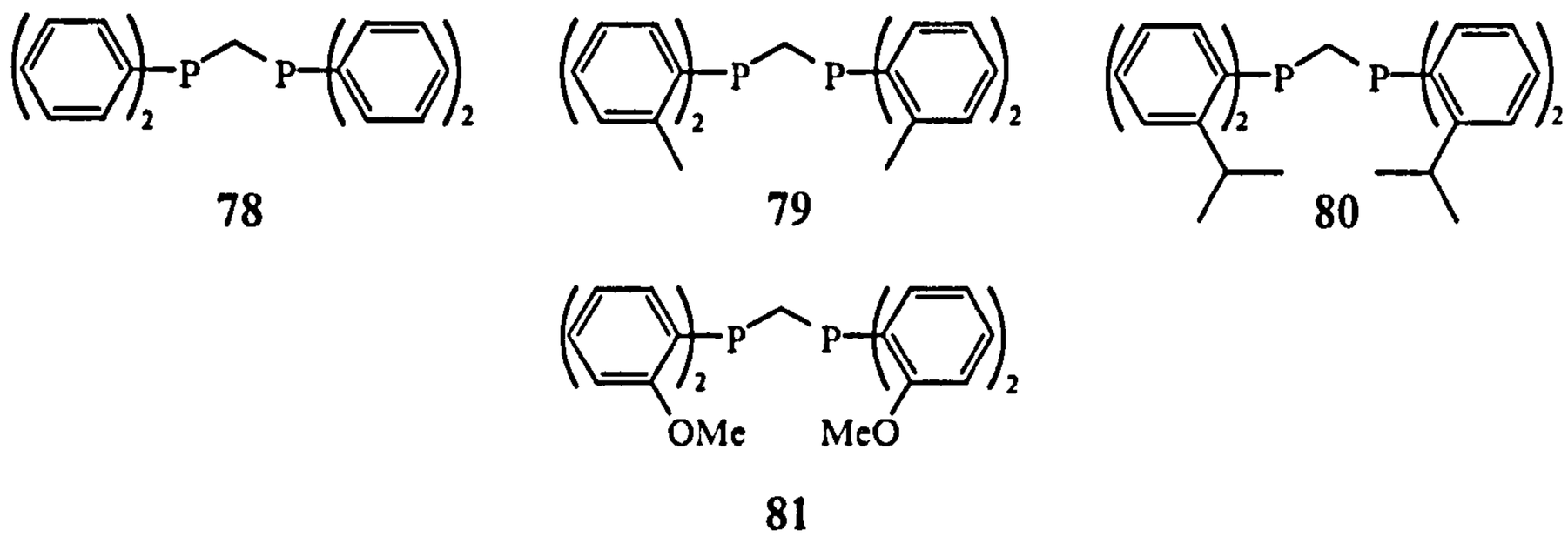


Figure 3.21 - Bis(diarylphosphino)ethane Ligands Tested for Isoprene Trimerisation

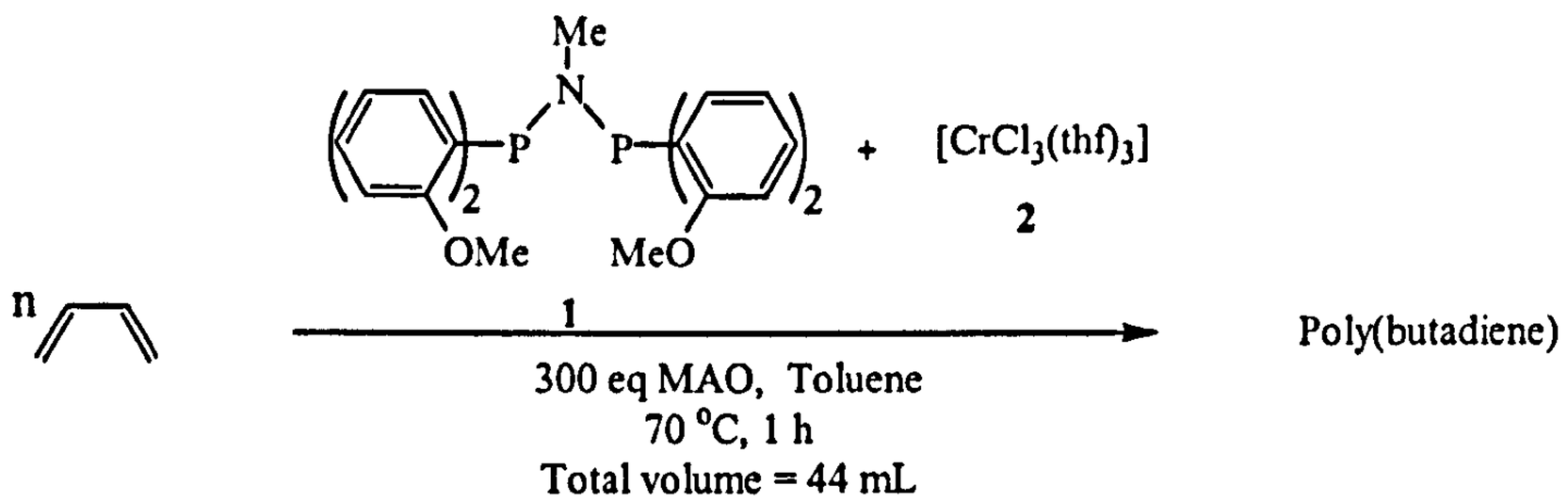
A selection of bis(diphenylphosphino)methane derivatives (Figure 3.21) were also tested for isoprene trimerisation and were found to be inactive. This may be because the carbon backbone is deprotonated during catalyst activation, causing the catalyst to become inactive or decompose.[4]

3.4. Trimerisation or Oligomerisation of other 1,3-Dienes

The $[CrCl_3(thf)_3]$/1/MAO system in Scheme 3.8 was also tested for 1,3-butadiene and 2,3-dimethyl-1,3-butadiene trimerisation.

3.4.1. 1,3 Butadiene

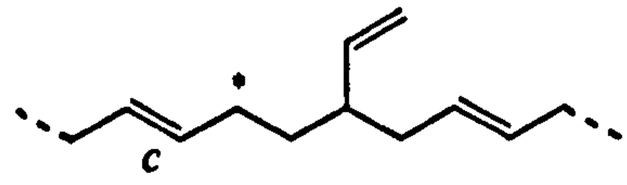
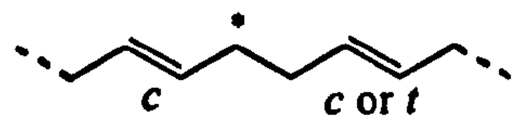
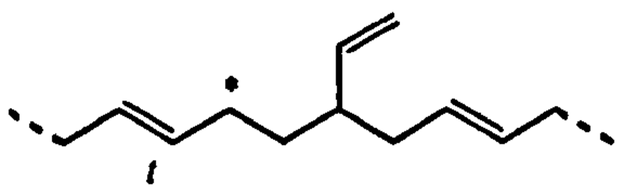
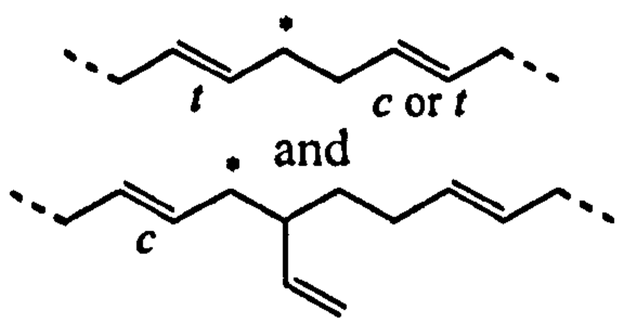
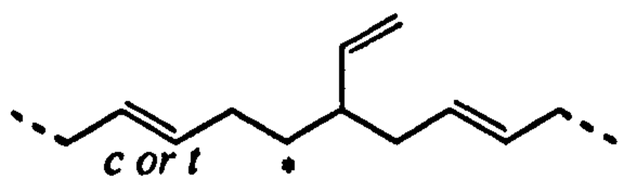
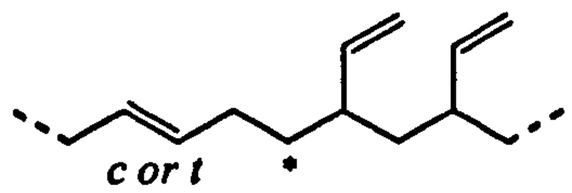
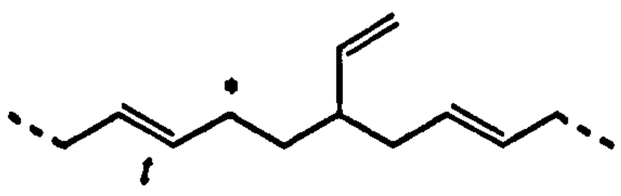
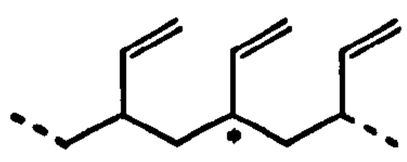
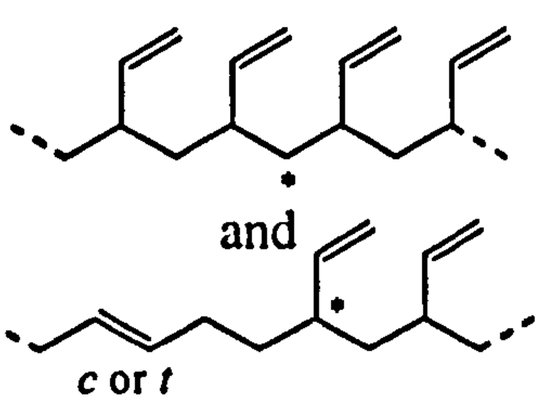
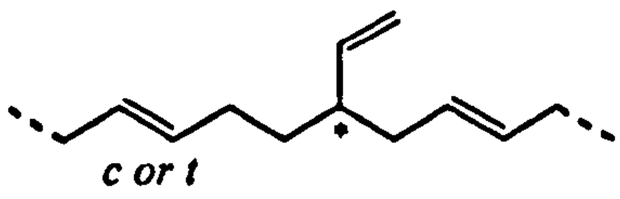
The trimerisation of 1,3-butadiene was attempted using the system shown in Scheme 3.15. Unlike isoprene, 1,3-butadiene is a gas so a different method was used to prepare the catalytic run. 1,3-Butadiene was bubbled through a solution of $[CrCl_3(thf)_3]$, ligand 1 and MAO in toluene for 10 minutes and then the reaction mixture was heated to 70 °C and stirred for 1 h.

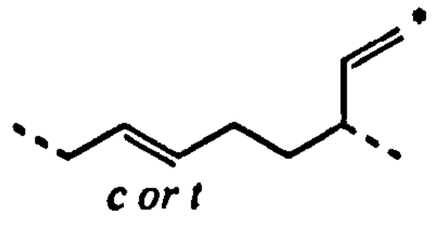
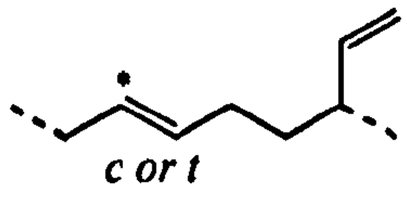
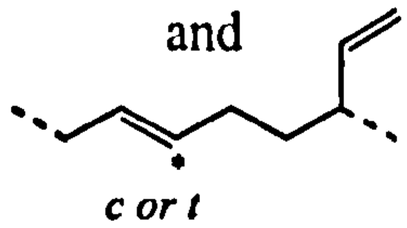
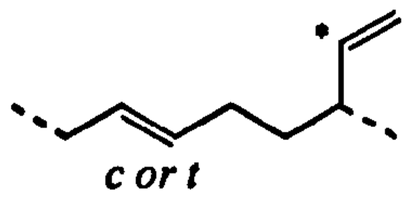


Scheme 3.15 – Polymerisation of 1,3-Butadiene

It was found that the system actually polymerised butadiene, with no oligomers observed in the GC trace. The polymer was isolated from the toluene solution by the addition of methanol. The ^{1}H and ^{13}C NMR spectra of the polymer were compared to literature values and from this the polymer structure was determined, the ^{13}C NMR spectrum for the polybutadiene is given in Table 3.11.[133 - 135]

Table 3.11 – ^{13}C NMR Spectrum Assignment of Polybutadiene[134]

Structure[a]	Chemical Shift δ / ppm		Percentage Integration / %
	Literature ($CDCl_3$)	Observed ($CDCl_3$)	
	25.3	25.2	1.6
	27.8	27.5	2.7
	30.6	30.2	2.0
	33.2	32.8	2.7
	34.5	34.3	1.0
	36.0	35.8	1.6
	38.7	38.6	7.5
	39.1	38.8	10.9
	40.5 – 42.4	40.1 – 42.4	19.9
	43.9	43.8	0.6

 *c or t*	114.8	114.4 – 115.1	20.7
 *c or t* and  *c or t*	130.1	129.5 – 130.7	9.4
 *c or t*	143.2	142.9 – 143.5	19.5

[a] * denotes carbon with which peak refers to and *c* is *cis* and *t* is *trans* double bonds.

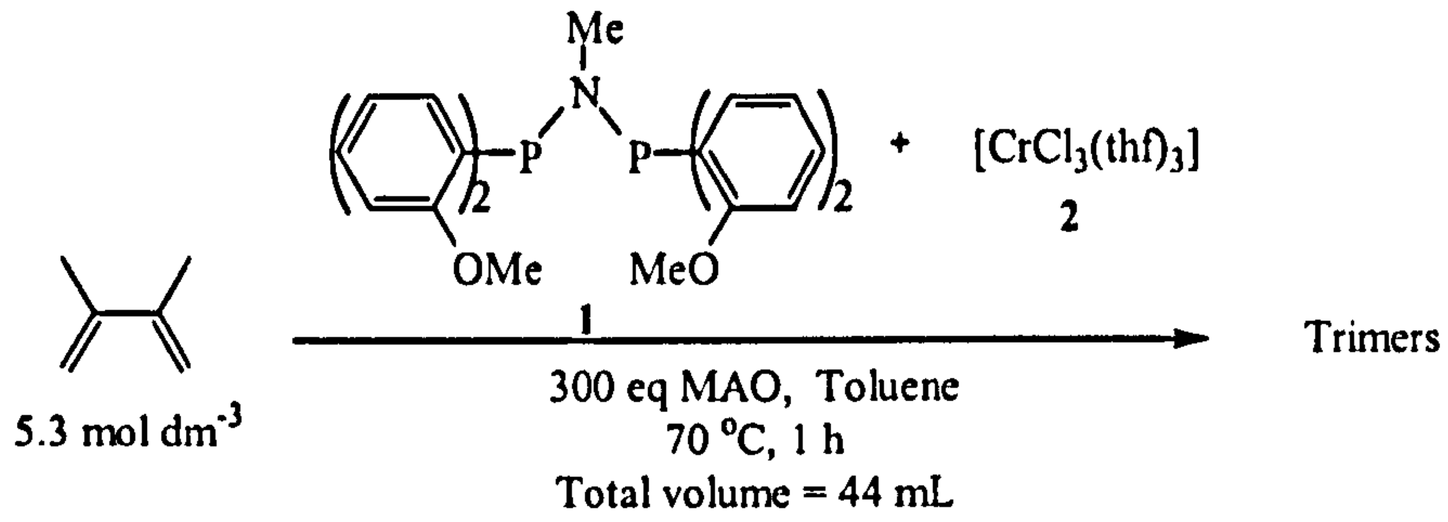
Table 3.13 shows the assignment of the ^{13}C NMR spectrum for the polybutadiene produced by the $[CrCl_3(thf)_3]$/1/MAO system, with the integration of each peak as a percentage. From this it was determined that the structure of the polymer was mainly a 1,2-monomer microstructure, with 60 % 1,2-, 33 % *cis* 1,4- and 7 % *trans* 1,4-monomer units.[134, 135] Molecular weight and polydispersity of the polymer is unknown due to the poor solubility of the polymer formed. A productivity of 1125 g (g Cr h)$^{-1}$ was obtained, which was calculated from the mass of polymer produced.

The polymerisation of 1,3-butadiene using chromium catalysts is known, such as $[Cr(acac)_3]$, with MAO as the activator.[135] Ricci and co-workers investigated a number of chromium catalysts with bidentate phosphine ligands with carbon backbones, which gave high activities and polybutadiene with a high percentage of 1,2 units.[136, 137] A system using $[CrCl_2(dmpm)_2]$ (dmpm = bis(dimethylphosphino)methane) with MAO gave 90 % 1,2-polybutadiene. This system was also shown to polymerise isoprene to give 3,4-polyisoprene.

3.4.2. 2,3-Dimethyl-1,3-butadiene

The trimerisation of 2,3-dimethyl-1,3-butadiene (DMB) was attempted using the system shown in Scheme 3.16. 0.04 mmol of $[CrCl_3(thf)_3]$ and 0.04 mmol of **1** were used, with 300 equivalents of MAO, 5.3 mol dm^{-3} of distilled 2,3-dimethyl-1,3-butadiene and

toluene as the solvent. As with the trimerisation of isoprene the reaction was run at 70 °C for 1 h. The results obtained from the trimerisation of 2,3-dimethyl-1,3-butadiene are shown in Table 3.12.

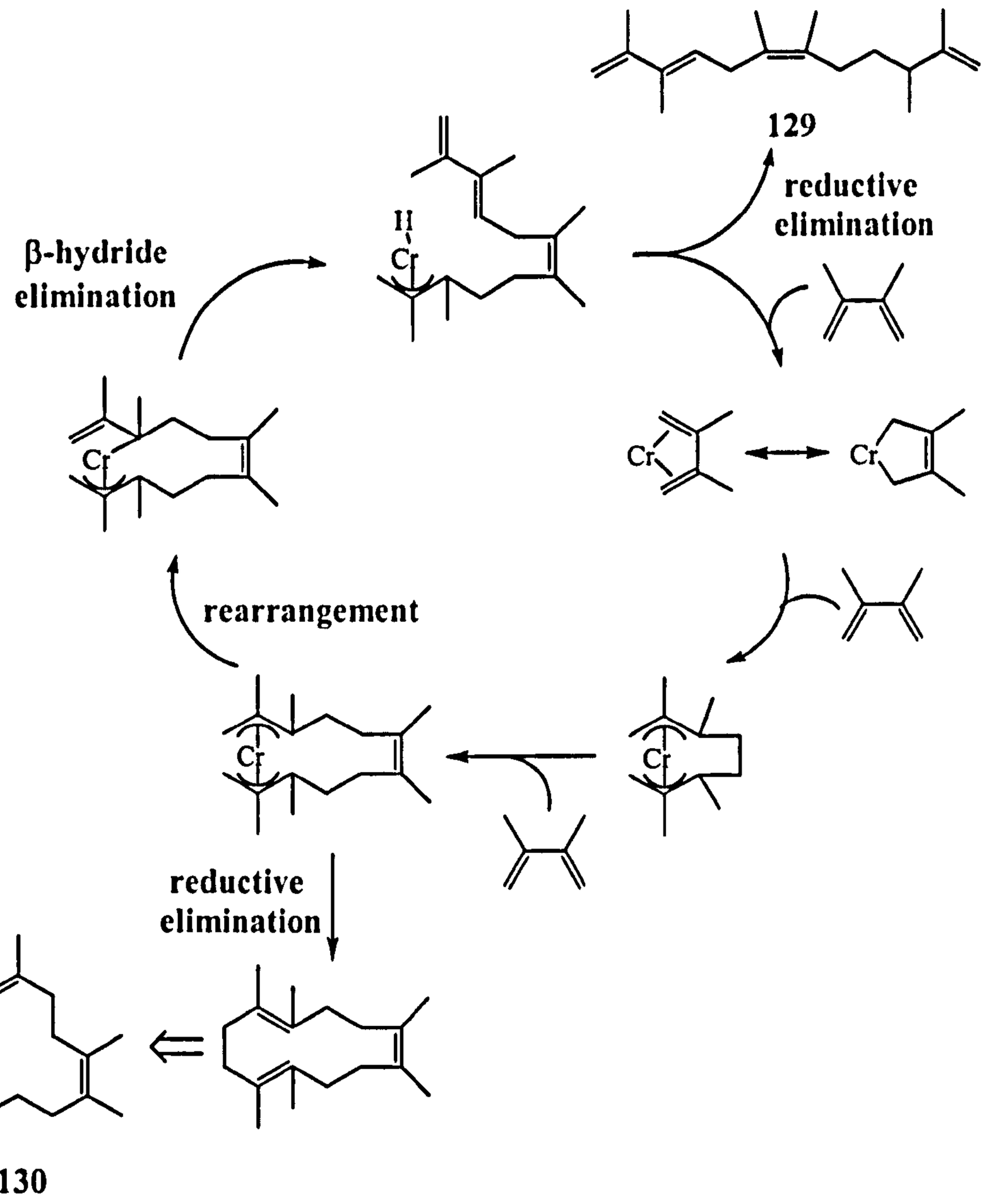


Scheme 3.16 – Trimerisation of 2,3-Dimethyl-1,3-Butadiene

Table 3.12 – Trimerisation of 2,3-Dimethyl-1,3-Butadiene

Run	DMB / mol dm^{-3}	Productivity / g (g Cr h)$^{-1}$	Product Distribution (wt %)	
			Trimers	Oligomers
3.34	5.3	1096	89.9	10.1

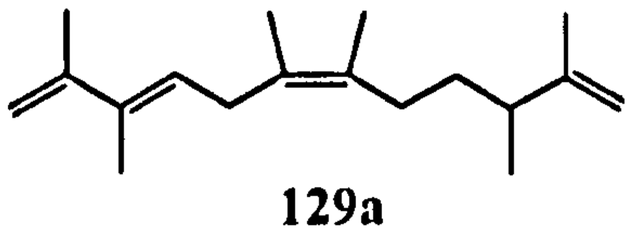
Table 3.12 shows that oligomerisation of 2,3-dimethyl-1,3-butadiene formed trimeric products in a high selectivity of 89.9 % and a productivity of 1096 g (g Cr h)$^{-1}$. The GC trace showed one peak for trimeric products and one peak for oligomeric products. Using the same mechanism as was used for isoprene trimerisation (Scheme 3.9 and 3.10) the possible isomers could be determined. This is shown on Scheme 3.17, unlike isoprene, where more than one route is possible, the mechanism for the trimerisation of 2,3-dimethyl-1,3-butadiene is much simpler, due to the symmetry of the monomer. Only one route is possible, reducing the total number of trimer isomers produced.



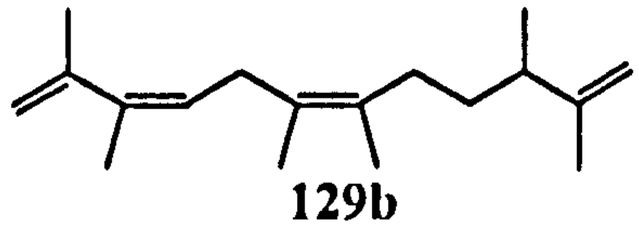
Scheme 3.17 – Formation of Trimers of 2,3-dimethyl-1,3-butadiene

The GC data showed that there was only one peak for trimer products and from Scheme 3.17 it can be seen that the trimer products are isomers of 2,3,6,7,10,11-hexamethyldodecatetraene, **129**. There are four different linear isomers of 2,3,6,7,10,11-hexamethyldodecatetraene, **129**, possible and one cyclic isomer, which are shown in Figure 3.22.

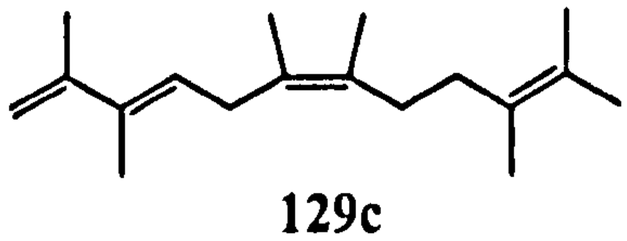
Linear Isomers



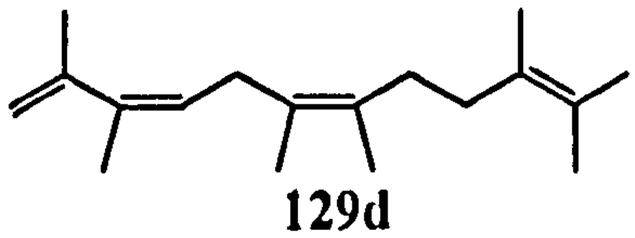
129a



129b



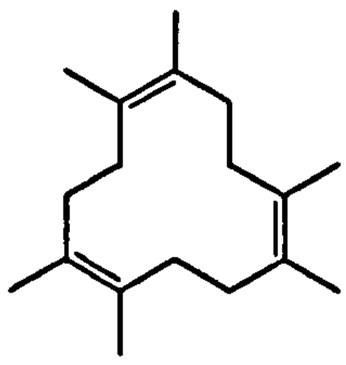
129c



129d

2,3,6,7,10,11-Hexamethyldodecatetraene

Cyclic Isomer



130

1,2,5,6,9,10-Hexamethyl-cyclododeca-1,5,9-triene

Figure 3.22 – Possible Isomers from Trimerisation of 2,3-dimethyl-1,3-butadiene

As previously stated, the GC trace of the trimerisation products contains one trimer peak, although this peak may be for more than one isomer which come at the same retention time. The cyclic isomer, **130**, has a higher boiling point than the linear isomers and so would have a different retention time, therefore if the trimer peak corresponded to the cyclic isomer, this would be the only isomer seen in the ^{13}C NMR spectrum of the products, shown in Figure 3.23. The ^{13}C NMR spectrum would contain six peaks due to the three fold symmetry of the ring and can therefore be ruled out as the ^{13}C NMR of the products contains eighteen main peaks. A ^{13}C 135 DEPT NMR experiment showed that the isomer contained six CH_3 groups, five CH_2 groups, two CH groups and five quaternary carbons. From this data it was hypothesised that the linear isomers present were isomers of 2,3,6,7,10,11-hexamethyl-1,3,6,11-dodecatetraene, **129a** and **129b**. It is not possible to suggest whether just one or both of these isomers is present.

In conclusion the trimerisation of 2,3-dimethyl-1,3-butadiene using the $[CrCl_3(thf)_3]$/**1**/MAO system formed either one or both of the *cis* or *trans* isomers of 2,3,6,7,10,11-hexamethyl-1,3,6,11-dodecatetraene.

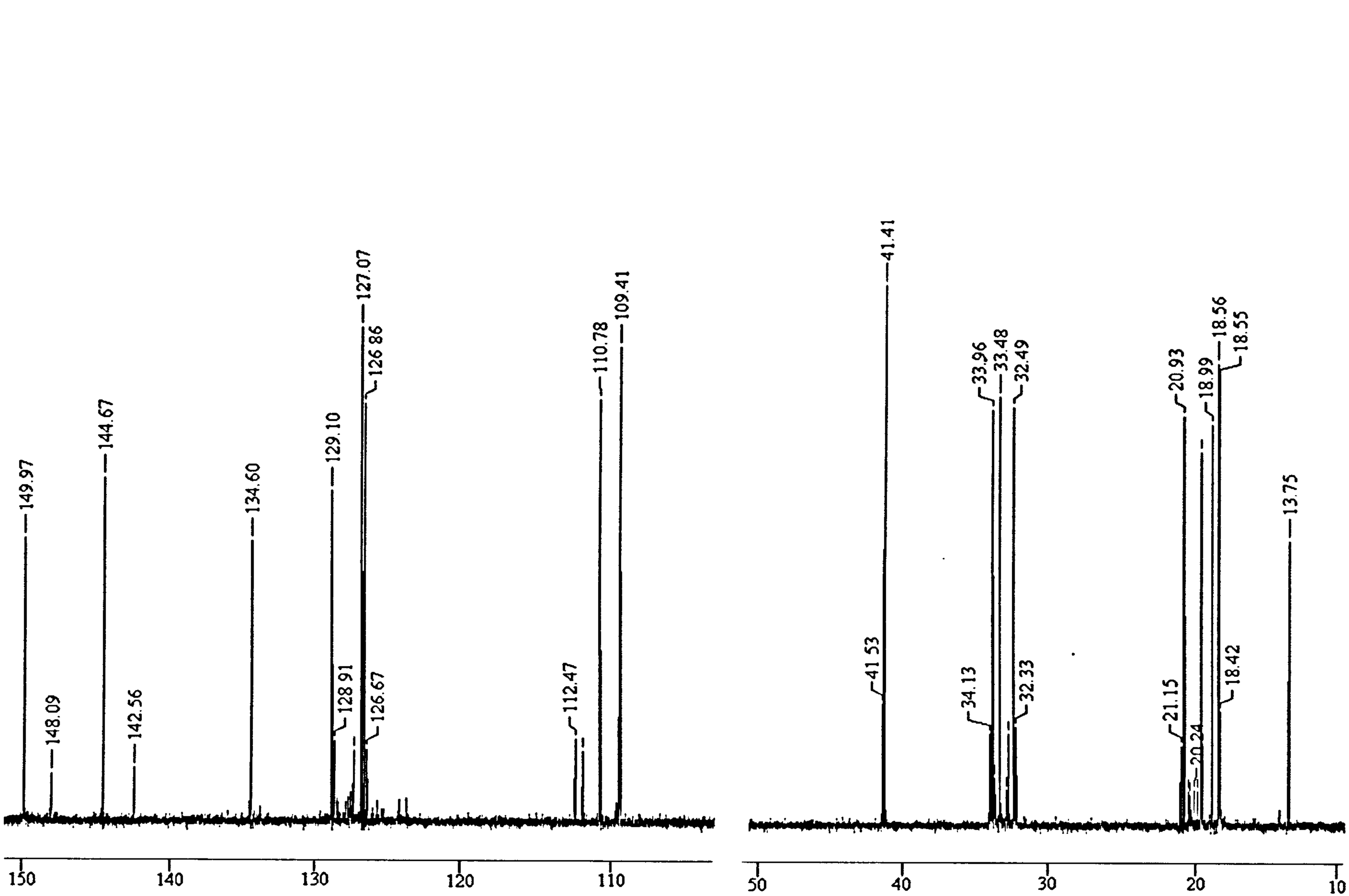


Figure 3.23 – ^{13}C NMR Spectrum of Products from Oligomerisation of 2,3-dimethyl-1,3-butadiene

3.5. Summary

In Chapter 2 the $[CrCl_3(thf)_3]$/**1**/MAO system was shown to cotrimerise ethene with styrene and is known to selectively trimerise ethene to 1-hexene.[4, 93] Therefore this system was tested for the trimerisation of 1,3-dienes. First to be tested was isoprene and it was found that the $[CrCl_3(thf)_3]$/**1**/MAO system was able to trimerise isoprene. Using 0.02 mmol of $[CrCl_3(thf)_3]$, 0.02 mmol of **1**, 300 equivalents of MAO, an isoprene concentration of 6.8 mol dm^{-3}, at 70 °C, a productivity of 826 g (g Cr h)$^{-1}$ was obtained, with a selectivity to the trimer products of 79.1 %. A selection of results from this chapter has been published.[130]

The possible trimer isomers were determined from looking at the mechanism, where isoprene inserts into the activated chromium centre to form a five membered chromametallacycle. This is followed by the insertion of two further isoprene units, to give a chromium diallyl species. Due to isoprene being unsymmetrical, insertion can occur *via* a 1,4 or 4,1 insertion, giving more than one possible route. The next stage can involve direct reductive elimination to give cyclic isomers, or rearrangement followed by β-hydride elimination and reductive elimination to give the linear isomers. From this it was discovered that there are 42 possible isomers. To reduce the number of isomer in the trimer mixture, the mixture was hydrogenated to give the corresponding alkanes. The ^{13}C NMR spectrum of the alkane mixture was compared to commercially available standards and from this is was found that the mixture contained one linear and one cyclic alkane isomer, which were determined to be 2,6,11-trimethyldodecane and 1,4,8-trimethylcyclododecane. These isomers come from the 1,4 insertion of isoprene into the mechanism, which is favoured due to the formation of the more stable 2-methyl-allyl group. Once the alkane structures were known, the isoprene trimers could be named as isomers of 2,6,11-trimethyldodecatetraene, **113** and 1,5,10-trimethyl-1,5,9-cyclododecatriene, **121**. It was not possible to determine to position of the double bonds on the linear isomers or state which of the eight possible isomers of **113** were formed.

The effects of changing reaction temperature, time and isoprene concentration were investigated. It was found that isoprene trimerisation only occurred above about 45°C

and gave the highest productivity at 70 °C. Productivity increased with isoprene concentration, with the ratio of cyclic to linear trimers also increasing. A range of ligands were tested and each of the successful ligands showed the same products as the system using ligand **1**. Increasing the size of the substituent on the nitrogen increased the selectivity to higher isoprene oligomers, whereas increasing the size of the substituent on the *ortho* position of the aryl group, increased the selectivity to isoprene trimers.

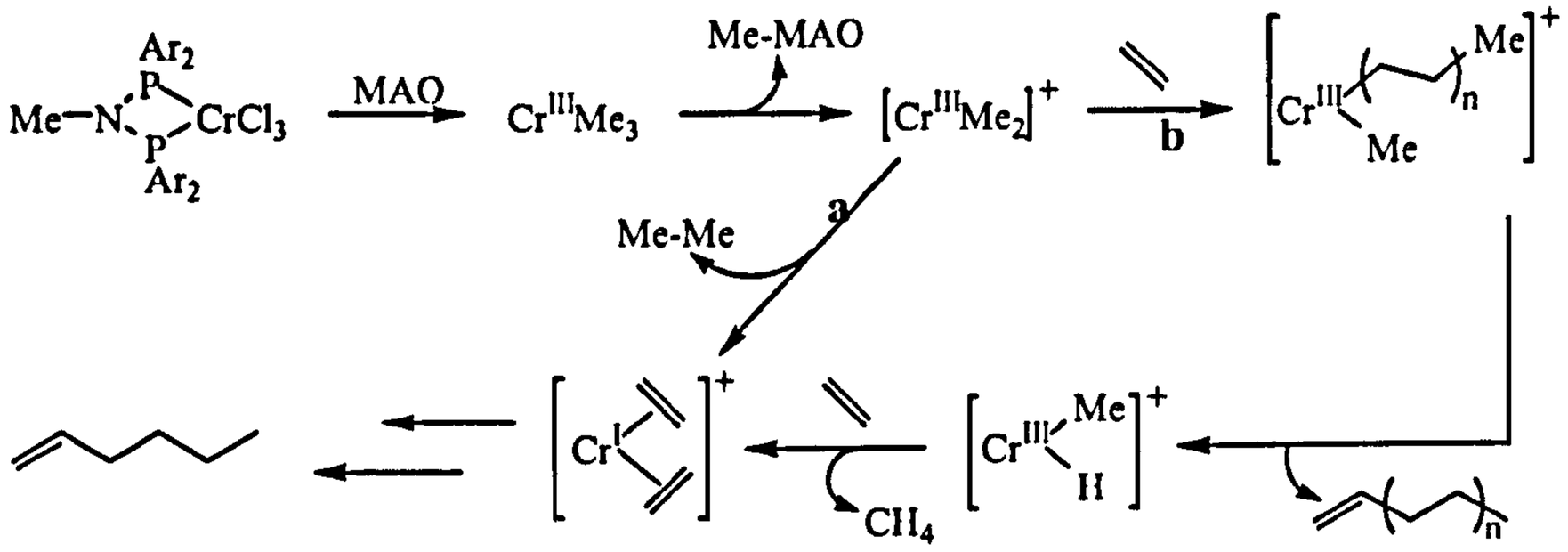
2,3-Dimethyl-1,3-butadiene and 1,3-butadiene were also used as substrates with the $[CrCl_3(thf)_3]$/**1**/MAO system. 2,3-Dimethyl-1,3-butadiene formed one trimer isomer and higher oligomers, with an 89.9 % selectivity to the trimer isomer. From the ^{13}C NMR spectrum of the trimer, it was found to be either one or both of the *cis* or *trans* isomers of 2,3,6,7,10,11-hexamethyl-1,3,6,11-dodecatetraene, **129a** or **129b**. 1,3-Butadiene formed polybutadiene with a productivity of 1125 g $(g\ Cr\ h)^{-1}$, consisting of 60 % 1,4 units. It is not known as to why this catalytic system switches between polymerisation and trimerisation for 1,3-dienes but these results suggest that the steric bulk of the ligand and the substrate have a large effect on the outcome. 1,3-Butadiene, which has no methyl groups, is the least bulky substrate and forms polymer. Whereas the most bulky substrate, 2,3-dimethyl-1,3-butadiene, with two methyl groups, selectively forms a trimeric product.

Chapter 4

Chromium(I) Carbonyl Phosphine Complexes in Ethene Trimerisation

4.1. Introduction

As stated in Section 1.4, Manyik and co-workers[7] and Kohn and co-workers[58] proposed a metallocycle mechanism for ethene trimerisation involving a Cr(I)/(III) system. In this mechanism the chromium precursor has an oxidation state of +III, which becomes +I upon activation. Two ethene molecules coordinate to the Cr(I) centre and undergo oxidative coupling to give the chromacyclopentane, with a Cr(III) centre. The Cr(I) centre is regenerated by reductive elimination of the chromacycloheptane, releasing 1-hexene. This is shown in Scheme 4.1.



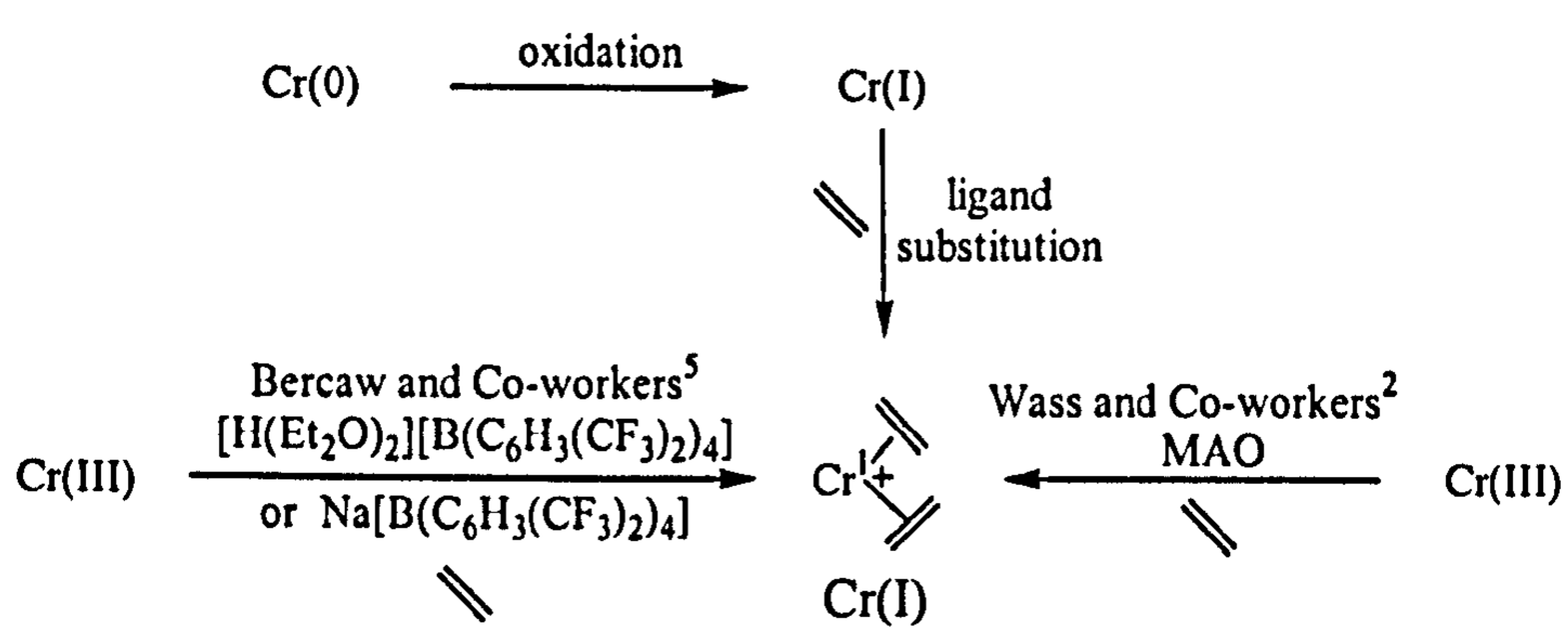
Scheme 4.1 – Activation of Chromium Catalyst by MAO, PNP Ligand has been Omitted for Clarity and Ar is o-OMeC$_6$H$_5$.

In the [$CrCl_3(thf)_3$]/1/MAO system the key Cr(I) di-alkene species is believed to be produced by methylation of the trichloride precursor, followed by methide abstraction and reductive elimination of ethane.[1, 4] Bercaw and co-workers have evidence for this mechanism by synthesising [$CrPh_3$(**1**)], **7**, and [CrBr(*o*,*o*'-biphenyldiyl)(**1**)], **33**. Upon activation of compound **33** (Scheme 1.22) with Na[$B(C_6H_3(CF_3)_2)_4$], or [$CrPh_3$(**1**)], **7** with [$H(Et_2O)_2$][$B(C_6H_3(CF_3)_2)_4$], followed by exposure to ethene, 1-hexene was produced in comparable productivities and selectivities to the [$CrCl_3(thf)_3$]/1/MAO system (see Scheme 1.15). From this work the activation of the Cr(III) catalyst with MAO can be extended, as shown in route **b** in Scheme 4.1, where ethene coordinates to the chromium centre and inserts into the Cr-Me bond. This is followed by β-hydride elimination and reductive elimination to give the Cr(I) species. This group reported the synthesis of chromium carbonyl PNP complexes such as [$Cr(CO)_4(Ar_2PN(Me)PAr_2)$],

where Ar = (*o*-CD_3)-C_6H_5. These complexes were oxidised using $C_6H_5ICl_2$, Br_2 or I_2 to yield [Cr(PNP)X_3], Cr(III) complexes.[39]

McGuinness and co-workers previously investigated the use of alternative cocatalyst systems to MAO, such as $[Ph_3C][B(C_6F_5)_3]$ with $AlEt_3$.[52] It was reported that cocatalysts with large, weakly coordinating anions gave the highest productivities and selectivities, although these catalysts had shorter lifetimes. The research was then extended to aluminate systems to find catalyst systems with longer lifetimes, such as $[Ph_3C][Al(OC(CF_3)_3)_4]$. It was suggested that $AlEt_3$ is needed for alkylation of the Cr(III) centre and $[Ph_3C]^+$ is used as an alkyl abstracting agent.

As an alternative approach to generate an active catalyst, we propose a route involving the one electron oxidation of a Cr(O) species. This would be followed by ligand substitution to generate the Cr(I) di-alkene species (Scheme 4.1) and thus enter the catalytic cycle. The various different routes of catalyst activation are shown in Scheme 4.2.



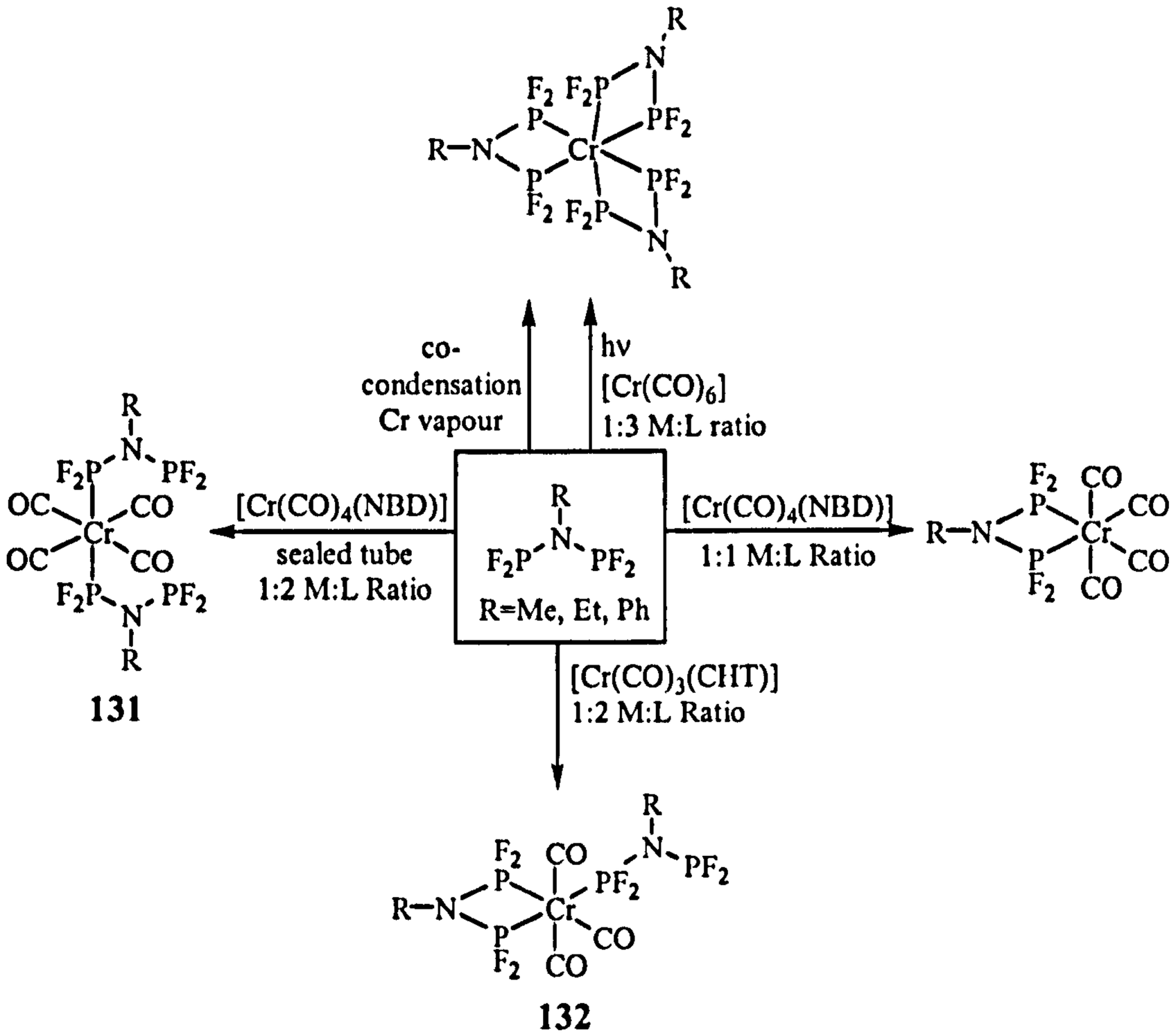
Scheme 4.2 – Routes to Formation of Cr(I) Di-alkene Species

4.1.1. Background to the Synthesis of Chromium Carbonyl Complexes

The synthesis of group 6 metal carbonyl *N,N*-bis(diarylphosphino)alkylamine (PNP) complexes was first described by Payne and co-workers.[139, 140] It was reported that the thermal reaction of PNP ligands with $[M(CO)_6]$ produced complexes with the formula $[M(CO)_4(PNP)]$, where M is molybdenum or tungsten. Nixon and co-workers[131] and King and co-workers[141-143] investigated the reaction of $F_2PN(R)PF_2$ ligands with group

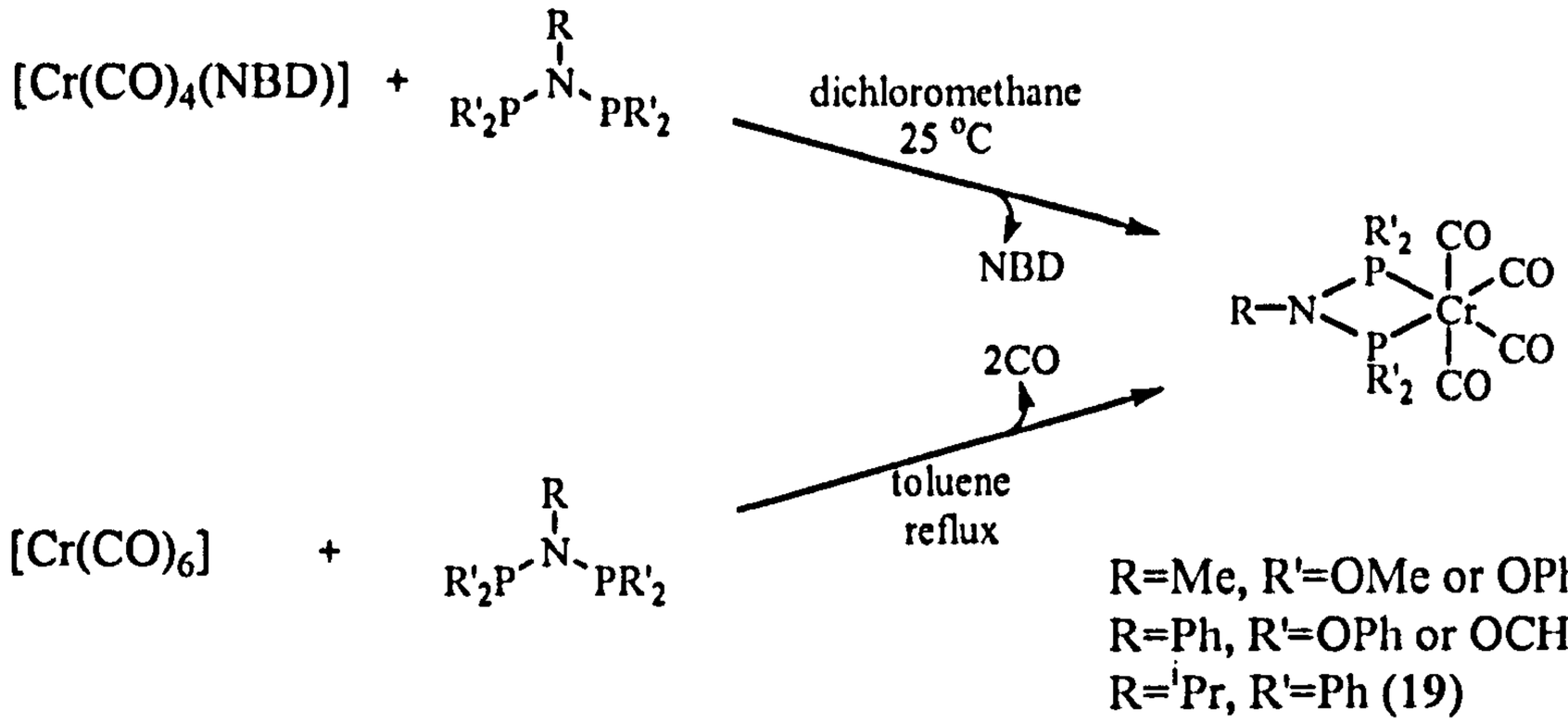
6 metal carbonyls (R = Me, Et or Ph). There methods were developed for the synthesis of metal carbonyl PNP complexes and the products given depended upon the method and ligand used. A selection of complexes and methods for synthesis are shown in Scheme 4.3 using $F_2PN(R)PF_2$ as the ligand.[144]

One method of synthesis is by displacement of a labile ligand such as norbornadiene (NBD) from $[Cr(CO)_4(NBD)]$ or cycloheptatriene (CHT) from $[Cr(CO)_3(CHT)]$. When two equivalents of the ligand is used, $[Cr(CO)_4(F_2PN(R)PF_2)_2]$, **131**, is formed, where each PNP ligand is coordinated to the metal centre via one phosphorus; or $[Cr(CO)_3(F_2PN(R)PF_2)_2]$, **132**, is formed, where one ligand is bidentate and the other is monodentate. Another route is photolysis, which is reacting the ligand with $[Cr(CO)_6]$ under ultraviolet light. A third route is co-condensation, where the ligand is reacted with chromium vapour. When $F_2PN(R)PF_2$ is used as the PNP ligand, both photolysis and co-condensation give $[Cr(F_2PN(R)PF_2)_3]$, where all of the CO ligands are displaced by PNP ligands. Reactions with molybdenum and tungsten were also reported with a wide range of possible complexes, including the formation of complexes with two or more metal centres.



Scheme 4.3 – Synthesis of Various Chromium Carbonyl ($F_2PN(R)PF_2$) Complexes

Balakrishna and co-workers reported the synthesis of a range of metal carbonyl PNP complexes.[145] PNP ligands with the formula $R'_2PN(R)PR'_2$ were investigated, where R and R' are: R=Me and R'=OMe or OPh; R=Ph and R'=OPh and OCH_2CF_3; R=*i*Pr and R'=Ph (Ligand **19**). The PNP ligand is reacted with either $[Cr(CO)_4(NBD)]$ or $[Cr(CO)_6]$, giving $[Cr(CO)_4(R'_2PN(R)PR'_2)]$, as shown in Scheme 4.4.



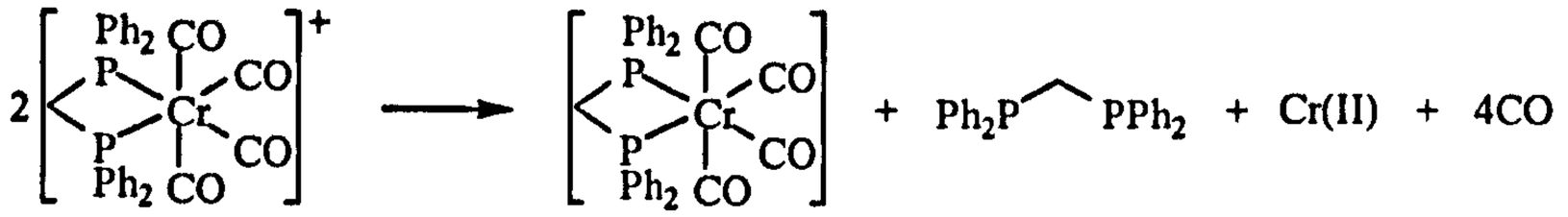
Scheme 4.4 – Synthesis of [Cr(CO)$_4$(R'$_2$PN(R)PR'$_2$)]

In one route, the PNP ligand was reacted with [Cr(CO)$_6$] in toluene under reflux for 30 h. In the second route PNP ligands were reacted with [Cr(CO)$_4$(NBD)] in dichloromethane at room temperature for 2 h. It was found that only one PNP molecule binds to the metal centre and no further displacement of CO is observed, even under reflux and the presence of excess ligand. Exposure of the [Cr(CO)$_4$(PNP)] complexes to ultra-violet light or the addition of trimethylamine-N-oxide (TMNO), in the presence of free ligand, did not lead to further CO replacement. The infrared (IR) spectra of these complexes showed four CO stretching frequencies in the range 2060 – 1890 cm^{-1}. The molybdenum and tungsten analogues of [Cr(CO)$_4$(PNP)] were also reported. The molecular structures of [Mo(CO)$_4$((PhO)$_2$PN(Ph)P(OPh)$_2$)] and [W(CO)$_4$(**19**)] (ligand **19** is Ph$_2$PN(*i*Pr)PPh$_2$) were given and showed an octahedral arrangement of ligands around the metal centre.[145]

4.1.2. Background to Oxidation of Cr(0) Complexes to Cr(I) Complexes

Connelly and co-workers showed that the oxidation of [Cr(CO)$_4$(dppe)] or [Cr(CO)$_4$(dppm)] produces a 17 electron species [Cr(CO)$_4$(dppe)]$^+$ or [Cr(CO)$_4$(dppm)]$^+$ which are isolable but unstable; it was suggested that the oxidation was a one electron reversible process.[146, 148] The group also found that the reaction of Ag[BF$_4$] with [Cr(CO)$_4$(dppm)] gives [Cr(CO)$_4$(dppm)][BF$_4$].[148] Bond and co-workers investigated the oxidation of a range of [Cr(CO)$_4$(PAr$_3$)$_2$] complexes, using [NO][PF$_6$] or Ag[ClO$_4$].[141] It was found that the oxidation of the complex can cause a rearrangement

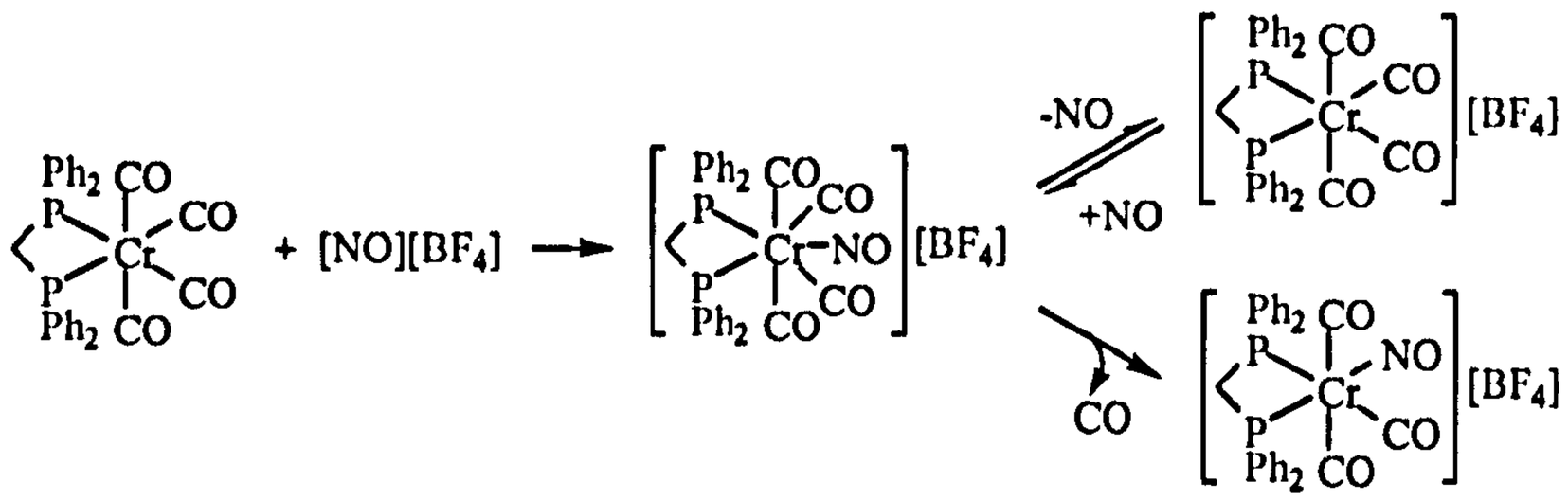
of ligands around the metal centre from a *cis* to *trans* conformation, although the product depended on the size and electronics of the ligand. It was suggested the *trans*-$[Cr(CO)_4(PAr_3)_2]$ configuration was favoured. This work was extended to geometrically constrained bidentate phosphine systems such as $[Cr(CO)_4(dppm)]$, cyclic voltammetry indicated that $[Cr(CO)_4(dppm)]$ undergoes a reversible one electron oxidation.[149] Oxidation of $[Cr(CO)_4(dppm)]$ using oxidative-controlled potential electrolysis gave $[Cr(CO)_4(dppm)]^+$, which was shown to decompose over time. The decomposition product was shown by IR spectroscopy to contain $[Cr(CO)_4(dppm)]$ and by ^{31}P NMR spectroscopy to contain free dppm. This suggests a disproportionation mechanism is occurring, as shown in Scheme 4.5.



Scheme 4.5 – Decomposition of [Cr(CO)$_4$(dppm)]

The oxidation of $[M(CO)_4L_2]$, where M = Cr, Mo, W and L = monodentate ligand, to $[M(CO)_4L_2]^+$ is more stable that for $[M(CO)_4(L\text{-}L)]$, where L-L is a bidentate ligand.[150] This is because for $[M(CO)_4L_2]^+$ the *trans* configuration is favoured over the *cis* configuration. $[M(CO)_4(L\text{-}L)]$ is geometrically constrained to the *cis* configuration and therefore, when oxidised, the complex cannot rearrange to form the more stable *trans* configuration. This means that the bidentate complexes may be more likely to undergo side reactions to relieve the strain, making $[M(CO)_4(L\text{-}L)]^+$ more reactive and less stable than $[M(CO)_4L_2]^+$.

Connelly and co-workers investigated the oxidation of chromium carbonyl phosphine complexes with $[NO][BF_4]$.[151] It was found that under certain conditions NO replaces a CO ligand, as shown in Scheme 4.6.



Scheme 4.6 – Reaction of [Cr(CO)$_4$(dppe)] with [NO][BF$_4$]

The IR spectra of *mer*-[Cr(CO)$_3$(NO)(dppm)][BF$_4$] contained the shift for NO at 1749 cm^{-1}, with CO stretches at 2025 cm^{-1} and 2089 cm^{-1}, showing that the oxidation of [Cr(CO)$_4$(dppe)] with [NO][BF$_4$], results in NO replacing a CO ligand, forming an 18 electron complex with a positive chromium centre and BF$_4$ as the anion.

In general the 18 electron chromium carbonyl diphosphine complexes can be oxidised to the 17 electron species but the product is unstable and decomposes back to 50 % of the equivalent amount of the 18 electron complex, as shown in Scheme 4.3.

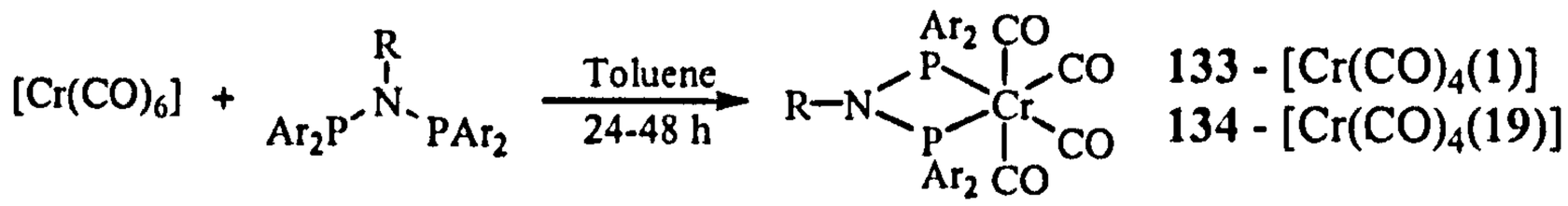
4.2. Objectives

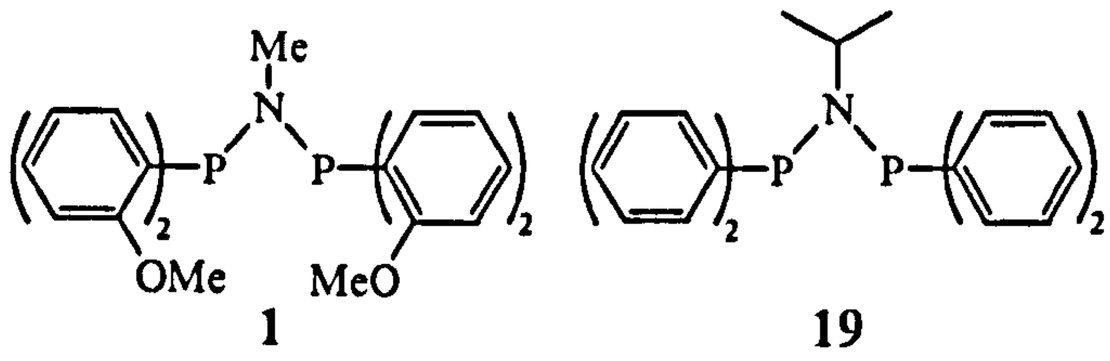
The objective of this chapter is to investigate the use of chromium (0) complexes as an alternative route into the active Cr(I) catalyst in the trimerisation of ethene. MAO suffers a number of drawbacks including its expense, incompatibility with polar substrates and difficulty in studying the active species; the discovery of new activation methods therefore has potential advantages. The oxidation of chromium (0) complexes to Cr(I) species may be a new, MAO free, route to the active species. This route may also be used to further investigate the mechanism for ethene trimerisation.

4.3. Chromium(0) Carbonyl Complexes

4.3.1. Synthesis of Chromium(0) Carbonyl Complexes

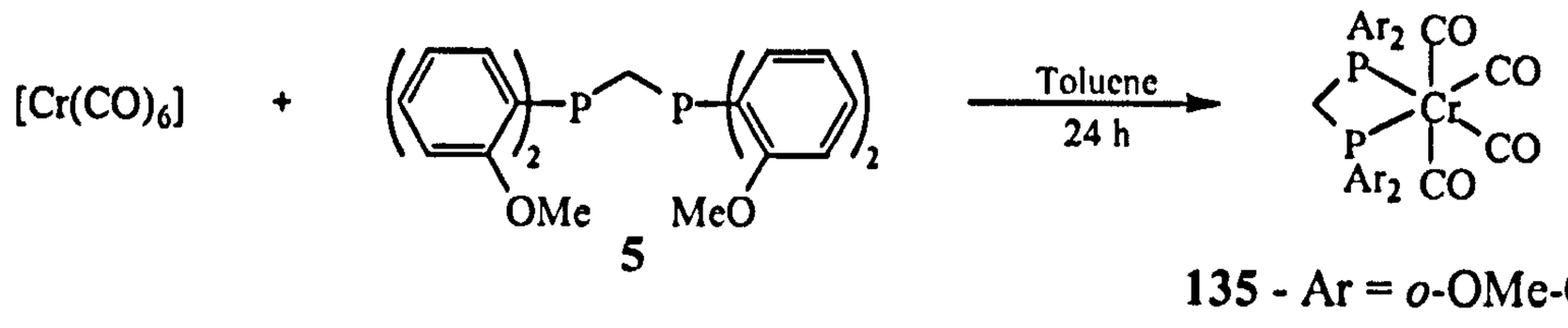
Chromium carbonyl complexes were synthesised using a method reported by Balakrishna and co-workers.[145] Scheme 4.7 shows the method for the formation of $[Cr(CO)_4(1)]$, **133** and $[Cr(CO)_4(19)]$, **134**.





Scheme 4.7 – Synthesis of Chromium Carbonyl PNP Complexes

Two chromium (0) carbonyl PNP complexes were synthesised, $[Cr(CO)_4(1)]$, **133** and $[Cr(CO)_4(19)]$, **134**. $[Cr(CO)_4(5)]$ was also synthesised, where ligand **5** is the dppm analogue of ligand **1**, with a carbon backbone. Chromium hexacarbonyl, $[Cr(CO)_6]$, and the PNP ligand were dissolved in toluene under nitrogen and heated under reflux for 24 to 48 hours. The reaction was monitored by ^{31}P NMR spectroscopy. The synthesis of $[Cr(CO)_4(5)]$, **135**, is shown in Scheme 4.8.



Scheme 4.8 – Synthesis of [Cr(CO)$_4$(5)], 135

$[Cr(CO)_4(5)]$, **135** was synthesised using the same method as $[Cr(CO)_4(1)]$, **133** and $[Cr(CO)_4(19)]$, **134**. The ^{31}P NMR data for complexes **133**, **134** and **135** is shown in Table 4.1.

Table 4.1 – ^{31}P NMR Shifts for Synthesised Chromium Carbonyl Complexes

Ligand	^{31}P Shift / ppm
$[Cr(CO)_4(1)]$, **133**	102.0
$[Cr(CO)_4(19)]$, **134**	114.0
$[Cr(CO)_4(5)]$, **134**	19.9

^{31}P NMR data for complexes **133**, **134** and **135** is consistent with chromium carbonyl PNP and dppe complexes, with the ^{31}P NMR shift for $[Cr(CO)_4(dppm)]$ being 26.0 ppm.[152] The data shows a single peak for each complex, which is due to the two equivalent phosphorus atoms. The NMR data is also consistent with that reported for $[Cr(CO)_4(19)]$, **134** by Balakrishna and co-workers.[145]

4.3.2. Molecular Structures of Chromium Carbonyl PNP Complexes

This section reports the molecular structures of complexes **133**, **134** and **135**. The hydrogen atoms and solvent molecules are omitted from each structure for clarity. The molecular structures of complexes **133**, **134** and **135** were consistent with the molecular structures of $[Mo(CO)_4((OPh)_2PN(Ph)P(OPh)_2)]$ and $[W(CO)_4(19)]$ reported by Balakrishna and co-workers.[145]

The molecular structure of $[Cr(CO)_4(1)]$, **133**, is shown in Figure 4.1.

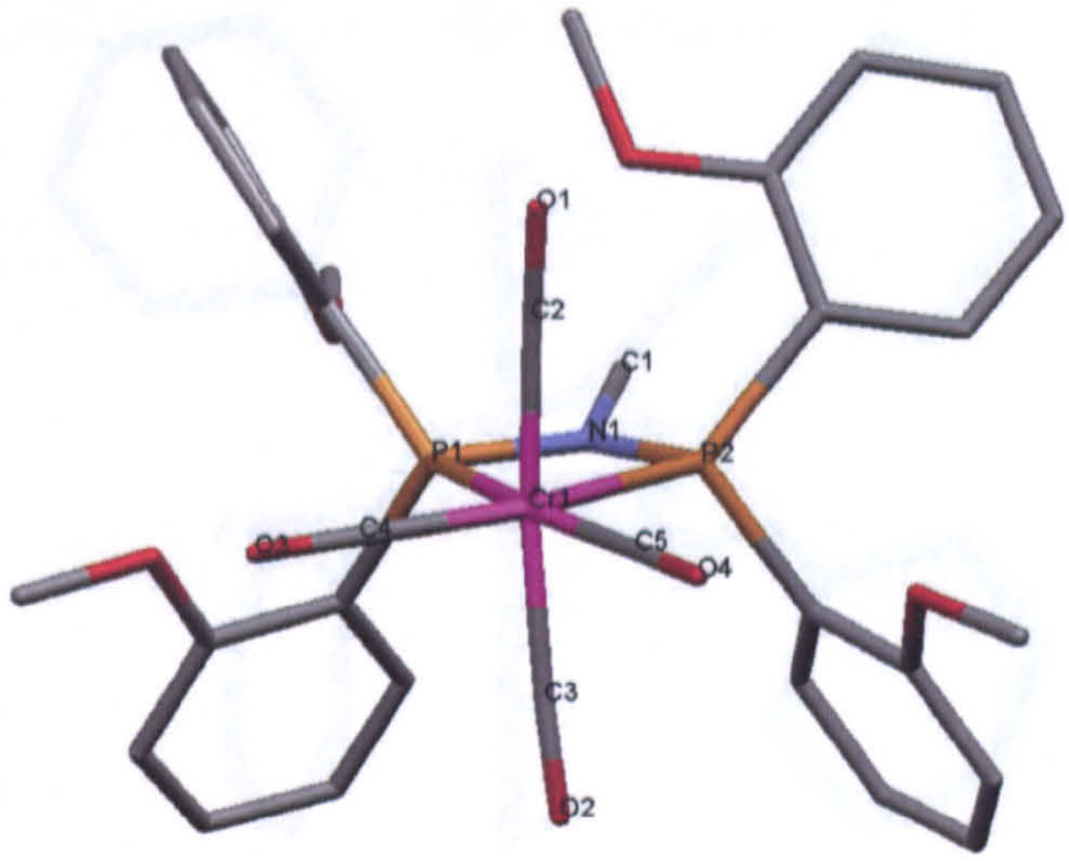


Figure 4.1 – Molecular Structure of [Cr(CO)$_4$(1)], 133

Yellow crystals of [Cr(CO)$_4$(**1**)], **133** were grown from dichloromethane at -30 °C. Complex **133** crystallises with one molecule of dichloromethane in the asymmetric unit and adopts an octahedral arrangement of ligands around the chromium centre. The complex has a fold angle of 2.6°, which is the difference between the CrP_2 plane and the P_2N plane, this implies that the Cr-P(1)-N(1)-P(2) plane is almost flat. The sum of the angles around the nitrogen atom is 356.6°, suggesting that the nitrogen is sp^2 hybridised and that the lone pair on the nitrogen is delocalised over the P(1)-N(1)-P(2) bonds. Also there is a short intra-molecular distance between O(7), in a methoxy group, and O(1), in a carbonyl group, of 3.02 Å. A selection of bond angles and lengths are given in Table 4.2.

The molecular structure of [Cr(CO)$_4$(**19**)], **134**, is shown in Figure 4.2.

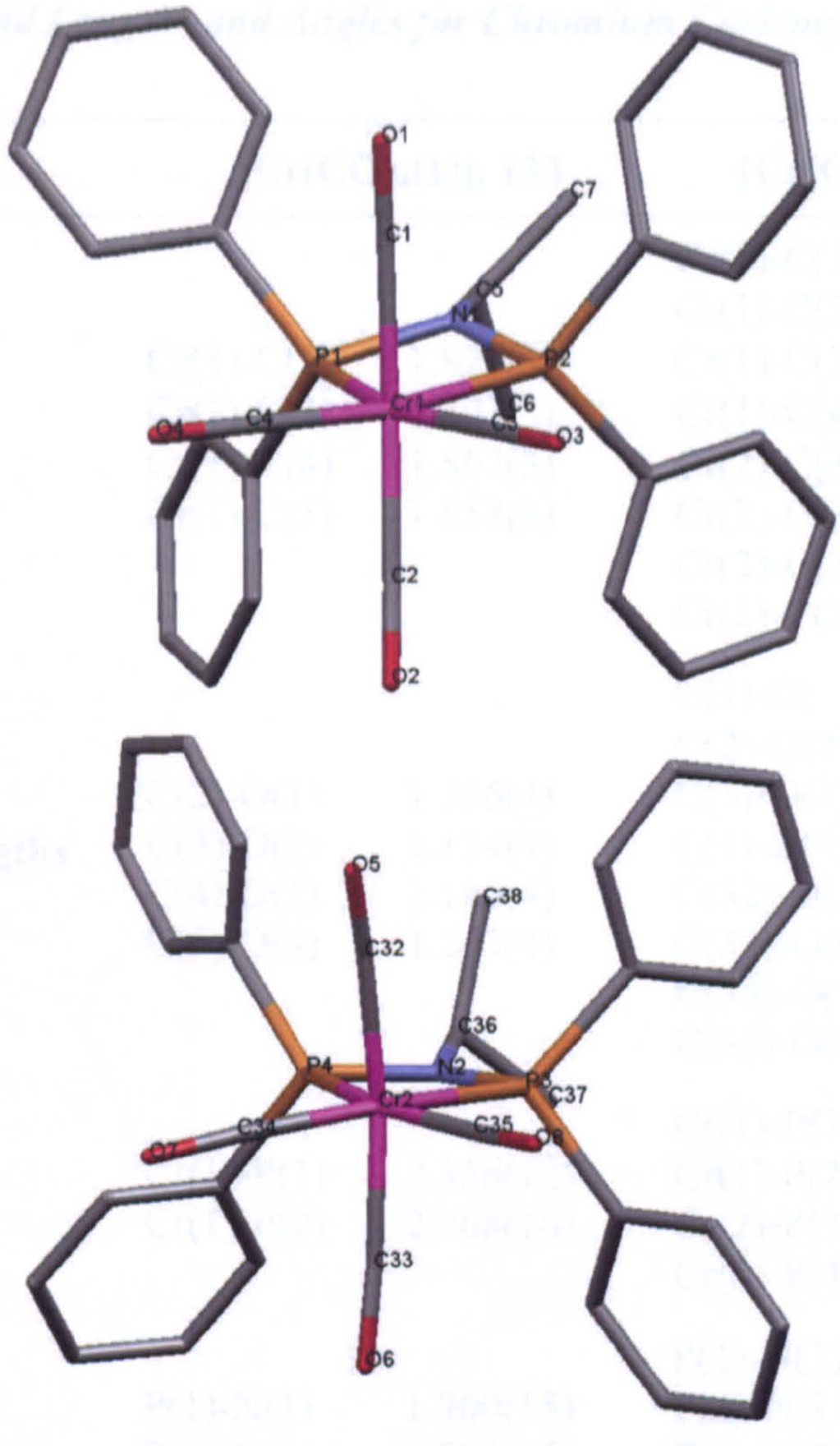


Figure 4.2 – Molecular Structure of [Cr(CO)$_4$(19)], 134

Complex **134** crystallises with two molecules in the asymmetric unit. The phenyl rings adopt a similar conformation in each molecule; with the difference appearing in the orientation of the isopropyl group. It is suggested that this is due to the difference in fold angle between the two molecules of 10.9° and 4.9°. The sum of the angles around the nitrogen atom is 356.9°, implying that, as with complex **133**, the nitrogen is sp^2 hybridised.

Table 4.2 – Bond Lengths and Angles for Chromium Carbonyl PNP Complexes

		[Cr(CO)$_4$(1)], 133		[Cr(CO)$_4$(19)], 134	
Bond Lengths / Å	Cr(1)-C(2)	1,878(3)	Cr(1)-C(1)	1,878(3)	
	Cr(1)-C(3)	1.891(3)	Cr(1)-C(2)	1.891(3)	
	Cr(1)-C(4)	1.862(3)	Cr(1)-C(3)	1.862(3)	
	Cr(1)-C(5)	1.858(3)	Cr(1)-C(4)	1.858(3)	
			Cr(2)-C(32)	1.885(3)	
			Cr(2)-C(33)	1.883(3)	
			Cr(2)-C(34)	1.858(3)	
			Cr(2)-C(35)	1.863(3)	
	C(2)-O(1)	1.156(4)	C(1)-O(1)	1.152(3)	
	C(3)-O(2)	1.154(4)	C(2)-O(2)	1.149(3)	
	C(4)-O(3)	1.146(4)	C(3)-O(3)	1.153(3)	
	C(5)-O(4)	1.155(4)	C(4)-O(4)	1.158(3)	
			C(32)-O(5)	1.156(3)	
			C(33)-O(6)	1.151(3)	
			C(34)-O(7)	1.150(3)	
			C(35)-O(8)	1.153(3)	
	Cr(1)-P(1)	2.356(12)	Cr(1)-P(1)	2.353(11)	
	Cr(1)-P(2)	2.368(10)	Cr(1)-P(2)	2.346(11)	
			Cr(2)-P(3)	2.326(9)	
			Cr(2)-P(4)	2.352(10)	
	P(1)-N(1)	1.700(15)	P(1)-N(1)	1.714(2)	
	P(2)-N(1)	1.704(15)	P(2)-N(1)	1.715(2)	
			P(3)-N(2)	1.715(2)	
			P(4)-N(2)	1.713(2)	
Angles / °	P(1)-Cr(1)-P(2)	68.45(3)	P(1)-Cr(1)-P(2)	67.82(4)	
			P(3)-Cr(2)-P(4)	67.87(3)	
	P(1)-N(1)-P(2)	102.04(13)	P(1)-N(1)-P(2)	99.86(11)	
			P(3)-N(2)-P(4)	99.44(11)	
C≡O IR Stretches / cm^{-1} (CH_2Cl_2)		1869, 1888, 1907, 2003		1889 (br), 1919, 2006	

The Cr-P and Cr-CO bonds of **133** do not differ significantly from **134**, suggesting that the effect of the methoxy group (**133**) is small. The Cr-CO bond lengths of the CO ligands *trans* to phosphine ligand are slightly shorter than the CO ligands *trans* to other CO ligands, which is due to the weaker *trans* effect of CO ligands over phosphines. The carbonyl stretching frequencies of both complexes are typical of chromium carbonyl phosphine complexes.[153] Complex **133** shows the expected four bands in the IR spectrum, although complex **134** only shows three bands, but this may be due to the

overlap of two bands. Complex **133** has lower carbonyl stretching frequencies (1869, 1888, 1907 and 2003 cm^{-1}) than complex **134** (1889, 1919 and 2006 cm^{-1}). This suggests that ligand **1** is more basic than ligand **19**, as a lower stretching frequency indicates that complex **133** has more back-bonding from the metal centre to the carbonyl groups than complex **134**. This may be due to the methoxy groups on ligand **1**. The P-N-P angle and P-Cr-P bite angle of **134** are slightly smaller than that of **133**, which may be due to ligand **1**, with OMe groups, being a more sterically demanding in **1** than the phenyl groups in ligand **19**.

The molecular structure of $[Cr(CO)_4(\mathbf{5})]$, **135** is shown in Figure 4.3. Hydrogen atoms and dichloromethane molecules are omitted for clarity.

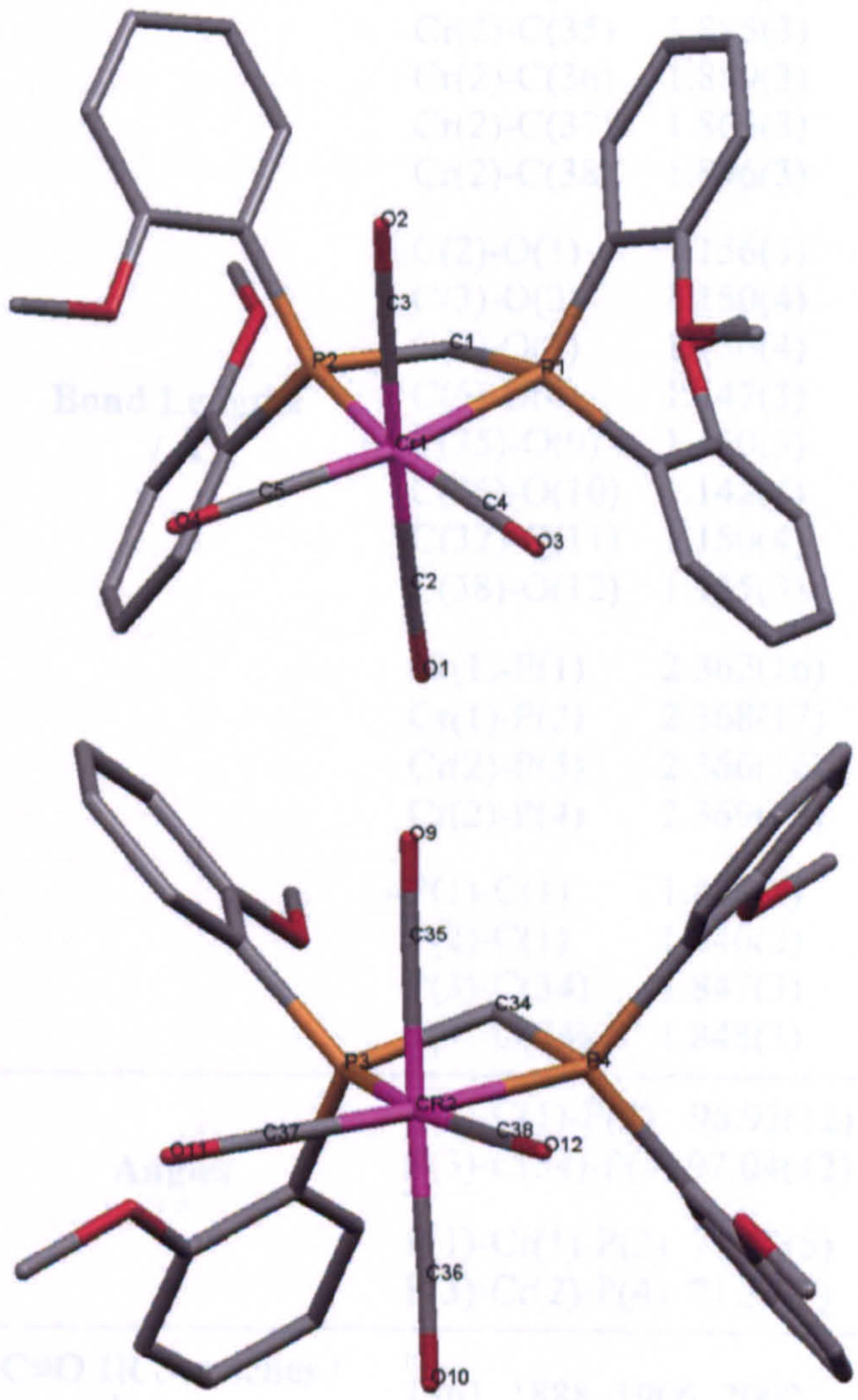


Figure 4.3 – Molecular Structure of $[Cr(CO)_4(5)]$, 135

As with [$Cr(CO)_4$(1)], **133**, [$Cr(CO)_4$(**5**)], **135** crystallises with two molecules in the asymmetric unit, with two molecules of dichloromethane. Two methoxy groups are on one face of the Cr-P-C-P plane pointing towards the metal centre. The other two OMe groups lie on the other side of the Cr-P-C-P plane, pointing away from the metal centre. Table 4.3 shows a selection of bond lengths and angles of [$Cr(CO)_4$(**5**)].

Table 4.3 – Selected Bond Angles and Lengths of [$Cr(CO)_4$(5)], 135

	[$Cr(CO)_4$(5)], 135	
Bond Lengths / Å	Cr(1)-C(2)	1.875(3)
	Cr(1)-C(3)	1.882(3)
	Cr(1)-C(4)	1.845(3)
	Cr(1)-C(5)	1.868(3)
	Cr(2)-C(35)	1.885(3)
	Cr(2)-C(36)	1.889(3)
	Cr(2)-C(37)	1.865(3)
	Cr(2)-C(38)	1.846(3)
	C(2)-O(1)	1.156(3)
	C(3)-O(2)	1.150(4)
	C(4)-O(3)	1.156(4)
	C(5)-O(4)	1.147(3)
	C(35)-O(9)	1.150(3)
	C(36)-O(10)	1.142(4)
	C(37)-O(11)	1.150(4)
	C(38)-O(12)	1.155(3)
	Cr(1)-P(1)	2.362(16)
	Cr(1)-P(2)	2.368(17)
	Cr(2)-P(3)	2.366(16)
	Cr(2)-P(4)	2.369(17)
	P(1)-C(1)	1.848(3)
	P(2)-C(1)	1.846(2)
	P(3)-C(34)	1.847(3)
	P(4)-C(34)	1.848(3)
Angles / °	P(1)-C(1)-P(2)	96.92(12)
	P(3)-C(34)-P(4)	97.04(12)
	P(1)-Cr(1)-P(2)	71.52(5)
	P(3)-Cr(2)-P(4)	71.55(5)
C≡O IR Stretches / cm^{-1} (CH_2Cl_2)	1861, 1888, 1906, 2002	

The Cr-P-C-P plane in **135** is less planar than complex Cr-P-N-P plane in complex **133**. The fold angles of the Cr-P-C-P rings are 16.9° and 15.8°, which is higher than complex **133**, although the Cr-P bond length is similar to the Cr-P bond in **133**. The P-C bond is smaller than the P-N bond in **133**, leading to a smaller P-C-P angle than the PNP analogue. Also the bite angle (P-Cr-P) angle is larger for complex **135** than **133** or **134**. The carbonyl stretching frequencies of complex **135** (1861, 1888, 1906 and 2002 cm^{-1}) are similar to that of complex **133** (1869, 1888, 1907 and 2003 cm^{-1}). This indicates that the nitrogen backbone of complex **133** is more electron rich than expected based on simple electronegativity arguments. This is likely to be due to the delocalisation of the nitrogen lone pair over the P-N-P chelate.

4.3.3. Cyclic Voltammetry of Complexes 133, 134 and 135

The oxidation of complexes **133, 134** and **135** was investigated by cyclic voltammetry, as shown in Figure 4.4. Cyclic voltammetry was conducted using a 1.0 x 10^{-3} mol dm^{-3} solution of the complex in dichloromethane, with a 0.1 mol dm^{-3} of $[NBu^n_4][PF_6]$ as the supporting electrolyte and $[Fe(\eta^5\text{-}C_5Me_5)_2]$ as the internal standard. $(E_p)_{red}$, $(E_p)_{ox}$ and $E^{0'}$ values are reported at a scan rate, v of 200 mV s^{-1} and versus a saturated calomel electrode (SCE).

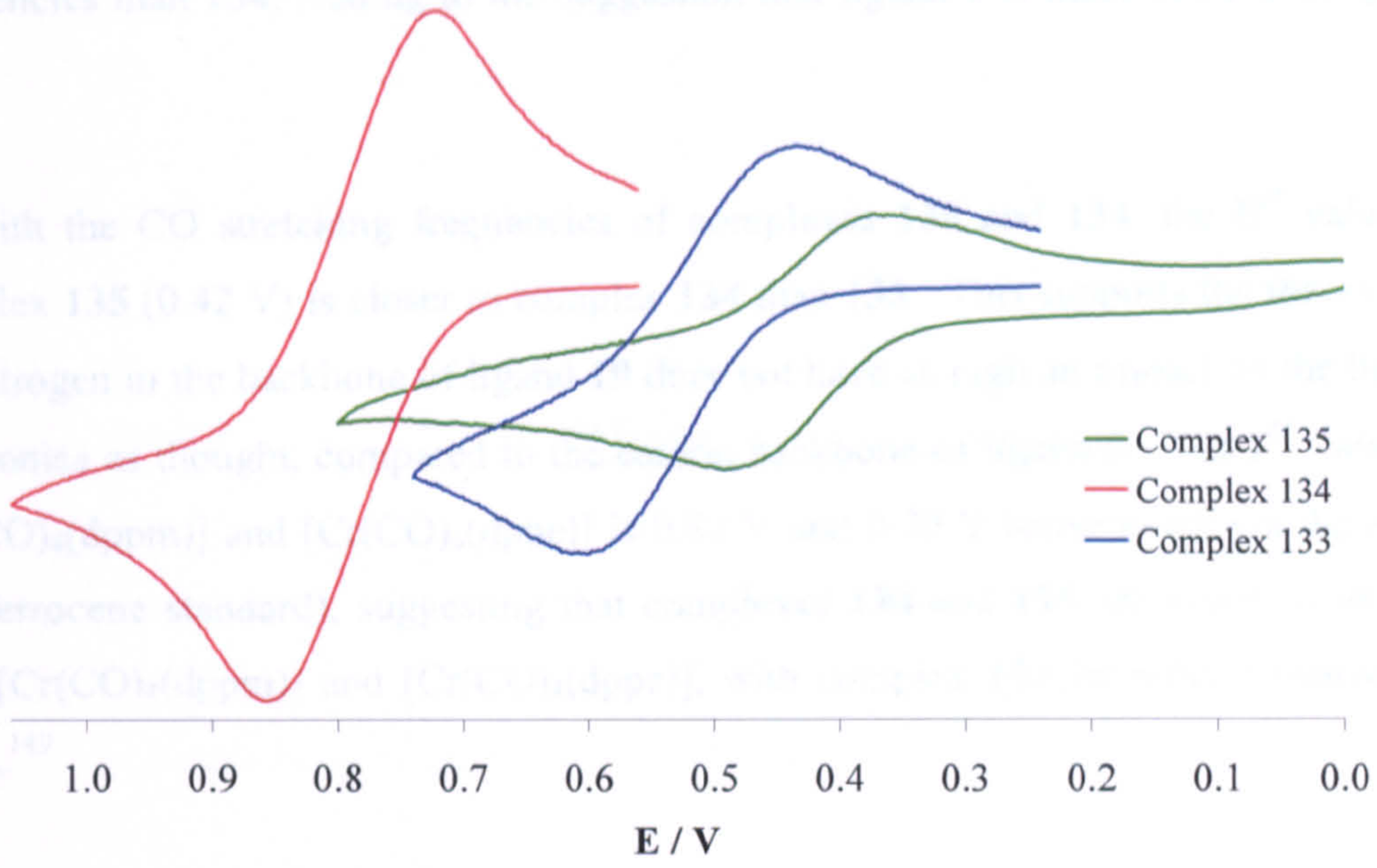


Figure 4.4 – Cyclic Voltammagram of Complexes 133, 134 and 135

Complexes **133**, **134** and **135** show a reversible oxidation. The $(E_p)_{red}$, $(E_p)_{ox}$ and $E^{0'}$ values for each complex is given in Table 4.4.

Table 4.4 - $(E_p)_{red}$, $(E_p)_{ox}$ and $E^{0'}$ Values For Synthesised Chromium Carbonyl Complexes

	$[Cr(CO)_4(\mathbf{1})]$, **133**	$[Cr(CO)_4(\mathbf{19})]$, **134**	$[Cr(CO)_4(\mathbf{5})]$, **135**
$E^{0'}$ / V	0.53	0.79	0.42
$(E_p)_{red}$ / V	0.61	0.86	0.35
$(E_p)_{ox}$ / V	0.45	0.72	0.49

Table 4.4 shows that complex **133** has a lower $E^{0'}$ value of 0.53 V than **134** (0.79 V), implying that **133** is easier to oxidise than **134**. This suggests that ligand **1** is more electron rich than ligand **19** and so σ-donation to the metal centre is higher, making the Cr centre more electron rich and so easier to oxidise. This is supported by the IR CO stretching frequencies in Section 4.4, where complex **133** had lower CO stretching

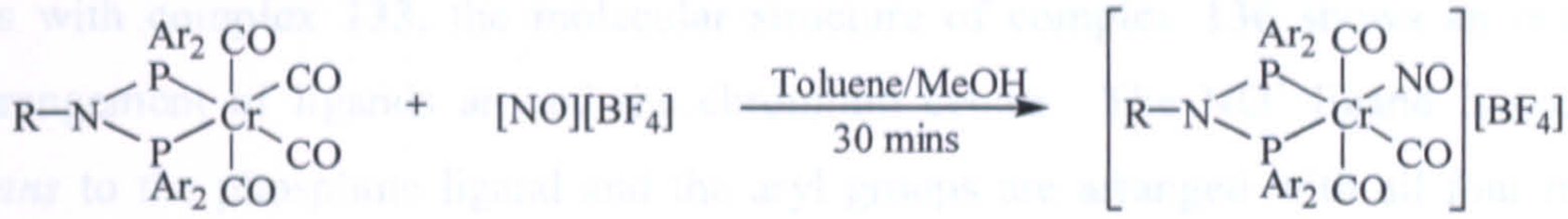
frequencies than **134**, leading to the suggestion that ligand **1** is more basic than ligand **19**.

As with the CO stretching frequencies of complexes **135** and **134**, the $E^{0'}$ value of complex **135** (0.42 V) is closer to complex **134** than **133**. This supports the theory that the nitrogen in the backbone of ligand **19** does not have as high an impact on the ligand electronics as thought, compared to the carbon backbone of ligand **5**. The $E^{0'}$ value of $[Cr(CO)_4(dppm)]$ and $[Cr(CO)_4(dppe)]$ is 0.80 V and 0.79 V respectively (vs Ag/AgCl and ferrocene standard), suggesting that complexes **134** and **135** are easier to oxidise than $[Cr(CO)_4(dppm)]$ and $[Cr(CO)_4(dppe)]$, with complex **133** showing a similar $E^{0'}$ value.[149]

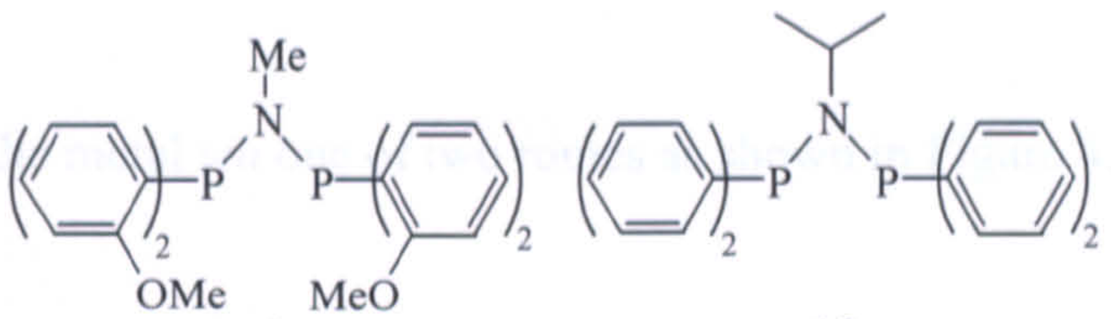
4.3.4. Chromium Nitrosyl Complexes

In order to use chromium carbonyl complexes for trimerisation of ethene, the metal centre must have a vacant site for ethene to bind. This requires the removal of carbonyl ligands and it was hypothesised that the substitution or removal of CO ligands would occur more readily if the back-bonding to each CO ligand from the metal centre is reduced. $[Cr(CO)_3(NO)(1)][BF_4]$, **136** is an 18 electron complex with an NO^+ ligand. The cationic nature of the complex results in less electron density on the chromium centre compared to the neutral analogue complex **133**. This reduces the π back-bonding to the carbonyl ligands, which in turn weakens the metal carbonyl bond; as a consequence substitution of the carbonyl ligands may be expected to occur more readily.

$[Cr(CO)_3(NO)(1)][BF_4]$, **136** was synthesised using a method developed by Connelly and co-workers, as shown in Scheme 4.9.[151]



136 - $[Cr(CO)_3(NO)(\mathbf{1})][BF_4]$
137 - $[Cr(CO)_3(NO)(\mathbf{19})][BF_4]$



Scheme 4.9 – Synthesis of $[Cr(CO)_3(NO)(PNP)][BF_4]$

$[Cr(CO)_3(NO)(\mathbf{1})]$, **136**, was synthesised by reacting $[Cr(CO)_4(\mathbf{1})]$ with nitrosyl tetrafluoroborate, $[NO][BF_4]$ in a mixture of toluene and methanol (10:1 ratio). It was found that using the mixed solvent system stabilised the formation of the chromium salt, **136**, compared with using only toluene. The complex was isolated by the addition of diethyl ether to precipitate a yellow solid.

Crystals of **136** were formed by slow diffusion of hexane into a concentrated dichloromethane solution of the complex at -30 °C. The molecular structure of $[Cr(CO)_3(NO)(\mathbf{1})]$, **136**, is shown in Figure 4.5.

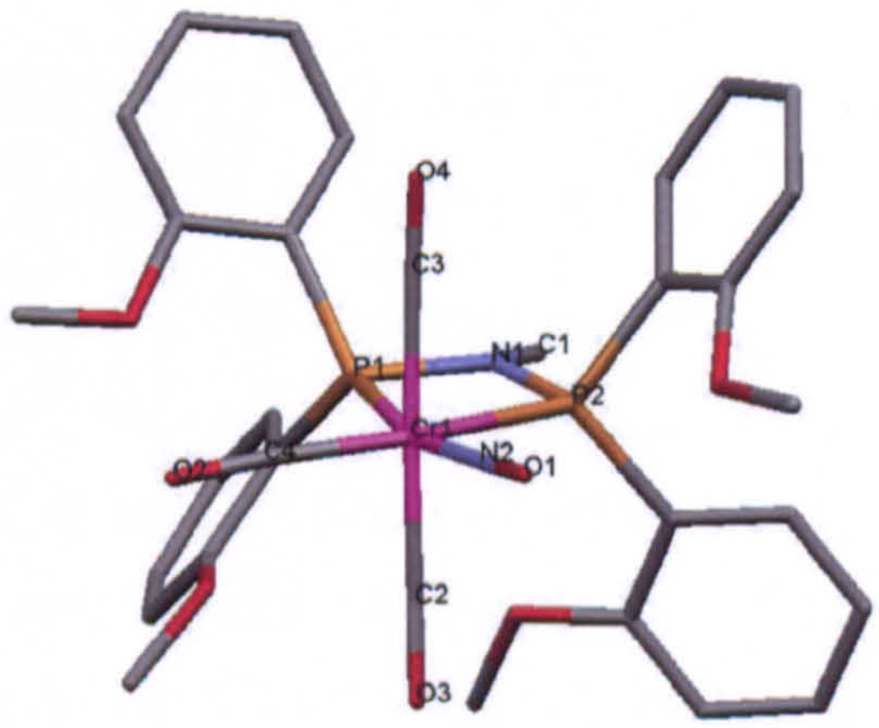


Figure 4.5 – Molecular Structure of $[Cr(CO)_4(NO)(1)]$, 136, Counterion Omitted for Clarity

As with complex **133**, the molecular structure of complex **136** shows an octahedral arrangement of ligands around the chromium centre. The NO^+ ligand is positioned *trans* to the phosphine ligand and the aryl groups are arranged with all four methoxy groups facing the metal centre. There is one molecule of the BF_4 counterion in the asymmetric unit.

NO can bond to the metal *via* one of two routes as shown in Figure 4.6.[154]

Figure 4.6 – Bonding Modes of the NO Ligand

In mode A the NO ligand acts a 3 electron donor to the metal centre, meaning that the Cr=N=O angle is between 160° and 180°. In mode B the NO ligand acts as a one electron donor to the metal centre where there is a lone pair on the nitrogen and the bond order of the N-O bond is 2. In complex **136** NO bonds in mode A, where the Cr(1)-N(2)-O(1) angle is 177.6°. A selection of bond angles and lengths are shown in Table 4.5.

Table 4.5 – Selected Bond Angles, Bond Lengths and IR Stretches of [Cr(CO)$_3$(NO)(1)], 136

	[Cr(CO)$_3$(NO)(1)], 136	
Bond Lengths / Å	Cr-C(2)	1.944(4)
	Cr-C(3)	1.928(4)
	Cr-C(4)	1.840(3)
	Cr-N(2)	1.774(3)
	C(2)-O(3)	1.137(4)
	C(3)-O(4)	1.132(4)
	C(4)-O(2)	1.132(4)
	N(2)-O(1)	1.164(3)
	Cr-P(1)	2.430(11),
	Cr-P(2)	2.382(9)
	P(1)-N(1)	1.700(2)
	P(2)-N(1)	1.693(2)
Short Intramolecular Distances / Å	N(2)-O(8)	2.953
	O(1)-O(8)	3.000
	O(3-O(7)	2.994
Angles / °	P(1)-Cr-P(2)	67.55(3)
	P(1)-N(1)-P(2)	104.07(13)
	Cr-N(2)-O(1)	177.6(3)
C≡O IR Stretches / cm^{-1} (CH_2Cl_2)	1755 (N≡O), 2024 (C≡O), 2091 (C≡O)	

The IR spectrum of complex **136** shows a stretch at 1755 cm^{-1} for the NO bond, which is typical of NO bonded to a metal.[154] The carbonyl stretching frequencies of complex **54** are higher than that of complex **133**, presumably due to the presence of the NO^+ ligand reducing the electron density of the metal centre. This in turn decreases the π-back-bonding to the π* orbital of the C≡O bond in each CO ligand. This is supported by the longer C≡O bond lengths and shorter Cr-C bond lengths in **136** compared to **133**. There are three short intramolecular distances between N(2)-O(8), O(1)-O(8) and O(3)-O(7) of 2.95 Å, 3.00 Å and 2.99 Å respectively. The Cr-P bonds in **136** are slightly

longer than in complex **133**, this is due to the *trans* effect of the NO^+ ligand in **136** compared to a CO ligand in **133**. The effect of the NO ligand is also shown in a longer Cr-P bond of 2.43 Å *trans* to the NO ligand, compared to 2.38 Å for Cr-P *trans* to CO and the Cr-NO bond is shorter than the Cr-CO bonds,. The Cr(1)-P(1)-N(1)-P(2) plane is flat with a fold angle of 2.4°. As with complex **133**, the nitrogen is in sp^2 hybridisation with the sum of the angles surrounding the nitrogen being 357.5°.

$[Cr(CO)_3(NO)(19)]$, **137**, was synthesised using the same method as complex **136**, as shown in Scheme 4.9, by reacting $[Cr(CO)_4(19)]$ with $[NO][BF_4]$ in a mix of toluene and methanol. The reaction was monitored by IR spectroscopy in dichloromethane and the data is shown in Table 4.6. X-ray quality crystals of this complex proved elusive.

Table 4.6 – IR Data of [Cr(CO)$_3$(NO)(19)], 137

Bond	IR Stretching Frequency / cm^{-1} (CH_2Cl_2)
N≡O	1760
C≡O	2022, 2092

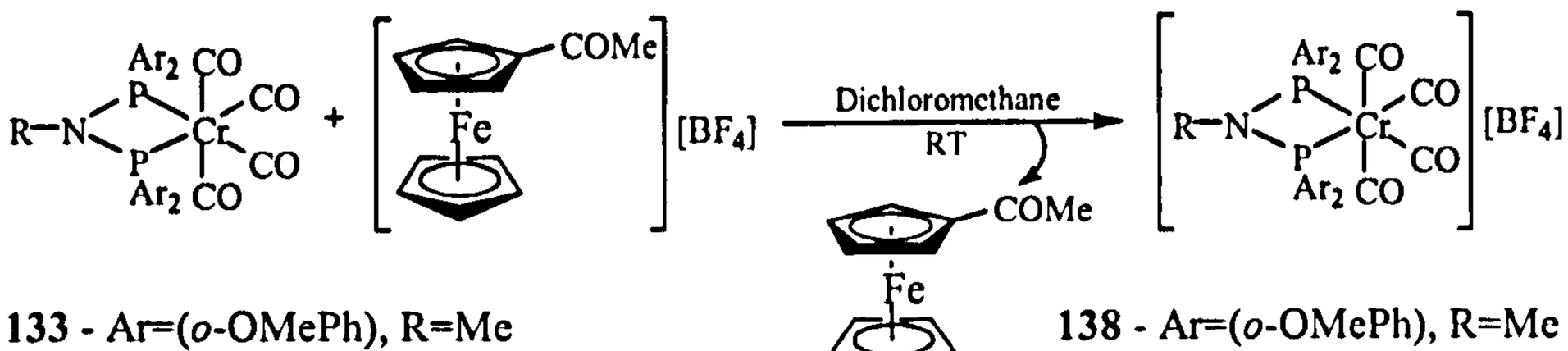
The IR spectrum of complex **137** shows a stretch at 1760 cm^{-1} for the NO bond, with carbonyl stretching frequencies of 2022 cm^{-1} and 2092 cm^{-1}. The IR carbonyl stretching frequencies of complexes **136** and **137** are similar. This suggests that compared to complexes **133** and **134**, the PNP ligand has less influence on the back-bonding from the metal centre to the carbonyl ligands in complexes **136** and **137**. Complex **136** was tested for ethene trimerisation and the results are reported in Section 4.5.

4.4. Chromium(I) Carbonyl Complexes

4.4.1. Oxidation with Acetyl Ferrocinium Tetrafluoroborate

The *in situ* oxidation of the chromium carbonyl PNP was investigated using a method reported by Connelly and co-workers.[148] The information from the cyclic voltammagram in Section 4.3.3 for the carbonyl complexes **133**, **134** and **135** indicated

that acetyl ferrocinium tetrafluoroborate $[Fe(\eta^5\text{-}C_5H_4(COMe))(\eta^5\text{-}C_5H_5)][BF_4]$ would oxidise the chromium (0) carbonyl PNP complexes to chromium (I) complexes. The method for oxidation of $[Cr(CO)_4(1)]$, **133**, $[Cr(CO)_4(19)]$, **134** and $[Cr(CO)_4(5)]$, **135**, is shown in Scheme 4.10.



133 - Ar=(*o*-OMePh), R=Me
134 - Ar=Ph, R=*i*Pr

138 - Ar=(*o*-OMePh), R=Me
139 - Ar=Ph, R=*i*Pr

Scheme 4.10 – Oxidation of 133 and 134 With $[Fe(\eta^5\text{-}C_5H_4(COMe))(\eta^5\text{-}C_5H_5)][BF_4]$

Complex **133** was reacted with $[Fe(\eta^5\text{-}C_5H_4(COMe))(\eta^5\text{-}C_5H_5)][BF_4]$ ([AcFe][BF_4]) in dichloromethane at room temperature. [AcFe][BF_4] is light sensitive, so the reaction vessels were covered with aluminium foil. The reaction shown in Scheme 4.10 was monitored by IR spectroscopy and the data is given in Table 4.7. The isolation of the oxidised products was unsuccessful as an insoluble black solid was obtained upon the removal of dichloromethane.

Table 4.7 – IR Data of $[Cr(CO)_4(1)][BF_4]$, 138 and $[Cr(CO)_4(19)][BF_4]$, 139

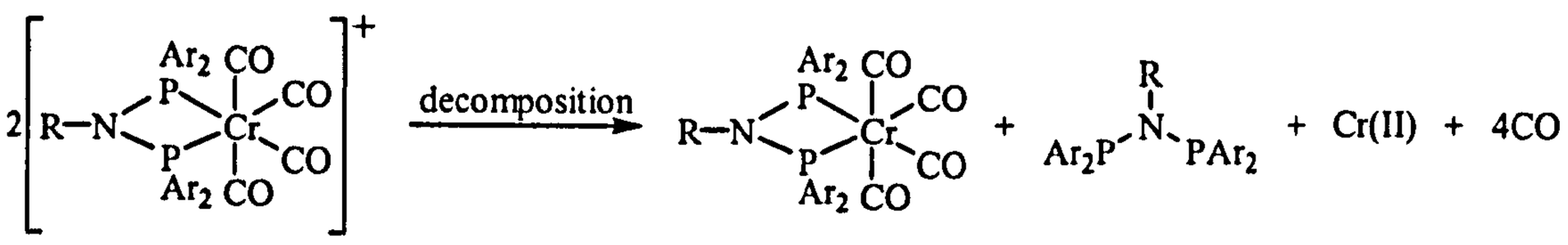
Complex	IR Carbonyl Stretching Frequencies / cm^{-1}
$[Cr(CO)_4(1)][BF_4]$, 138	1965, 2026, 2083
$[Cr(CO)_4(19)][BF_4]$, 139	1963, 2033, 2087

As expected the carbonyl stretches shift to a higher wavenumber upon oxidation of **133**, from 1869 cm^{-1}, 1888 cm^{-1}, 1907 cm^{-1} and 2003 cm^{-1} for $[Cr(CO)_4(1)]$, **50**, to 1965 cm^{-1}, 2026 cm^{-1} and 2083 cm^{-1} for $[Cr(CO)_4(1)][BF_4]$, **138**. This is a result of reducing the back-bonding to the π^* orbitals of the C≡O bonds upon oxidation from Cr(0) to Cr(I). This in turn shortens the bond length and strengthens the bond, meaning that more

energy is needed to vibrate the bond, producing a higher stretching frequency for the CO ligands in the IR spectrum.

The same pattern is seen for the oxidation of $[Cr(CO)_4(\mathbf{19})]$, **134**, with IR carbonyl stretches of 1889 (br) cm^{-1}, 1919 cm^{-1} and 2006 cm^{-1}, to $[Cr(CO)_4(\mathbf{19})][BF_4]$, **139**, with IR carbonyl stretches of 1963 cm^{-1}, 2033 cm^{-1} and 2087 cm^{-1}. The oxidation of $[Cr(CO)_4(\mathbf{5})]$, **135**, to $[Cr(CO)_4(\mathbf{5})][BF_4]$, was unsuccessful, although this may be because the product formed decomposed before the solution was analysed by IR spectroscopy. Decomposition may be due to the acidic methyl protons on the carbon backbone or cleavage of the P-C bond.[155]

The oxidation products **138** and **139** decomposed slowly over time under a nitrogen atmosphere, giving a half life of about 24 h at room temperature. These complexes are much more stable than the dppm or dppe analogues, with a half life of about four hours, showing that the oxidised PNP carbonyl complexes are more stable than the dppm analogues.[141, 149]



Scheme 4.11 - Decomposition of Complexes 138 and 139

The IR spectrum of the decomposed product shows the existence of complexes **133** and **134**, suggesting a disproportionation pathway (see section 4.1.2) is operating, as shown in Scheme 4.11. Where **138** or **139** decompose to give **133** and **134** respectively, along with free ligand, a Cr^{II} fragment and free CO. ^{31}P NMR of the decomposed product showed free ligand was present.

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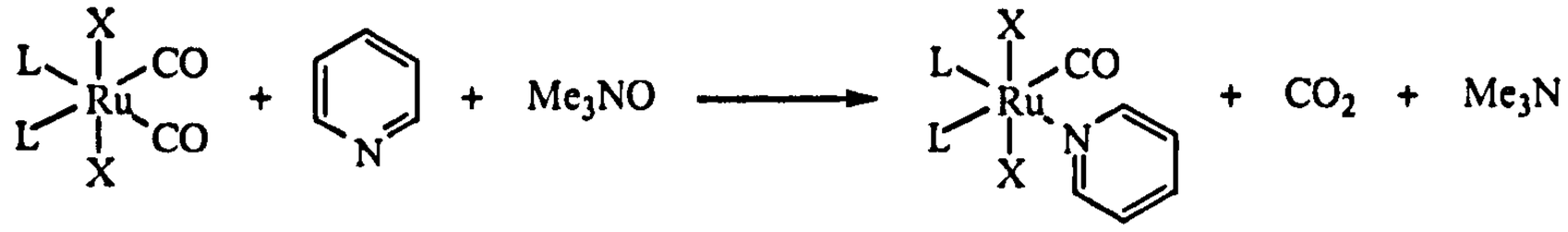
4.4.2. Attempted *In Situ* Reaction for Removing CO from Chromium Carbonyl Complexes using Amine Oxides

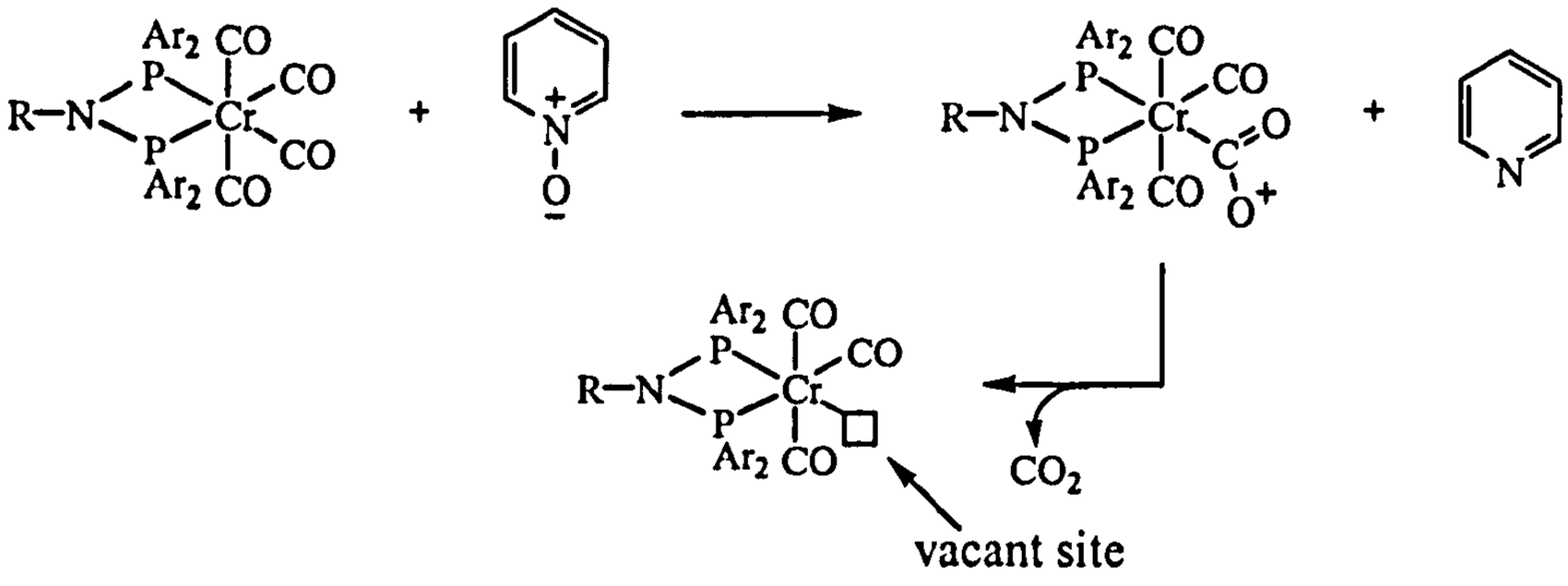
Using amine oxides to remove CO ligands is well known for metal complexes and an example is shown in Scheme 4.12.[156, 157]



Scheme 4.12 – Removal of CO by Addition of Trimethylamine-N-oxide (TMNO)

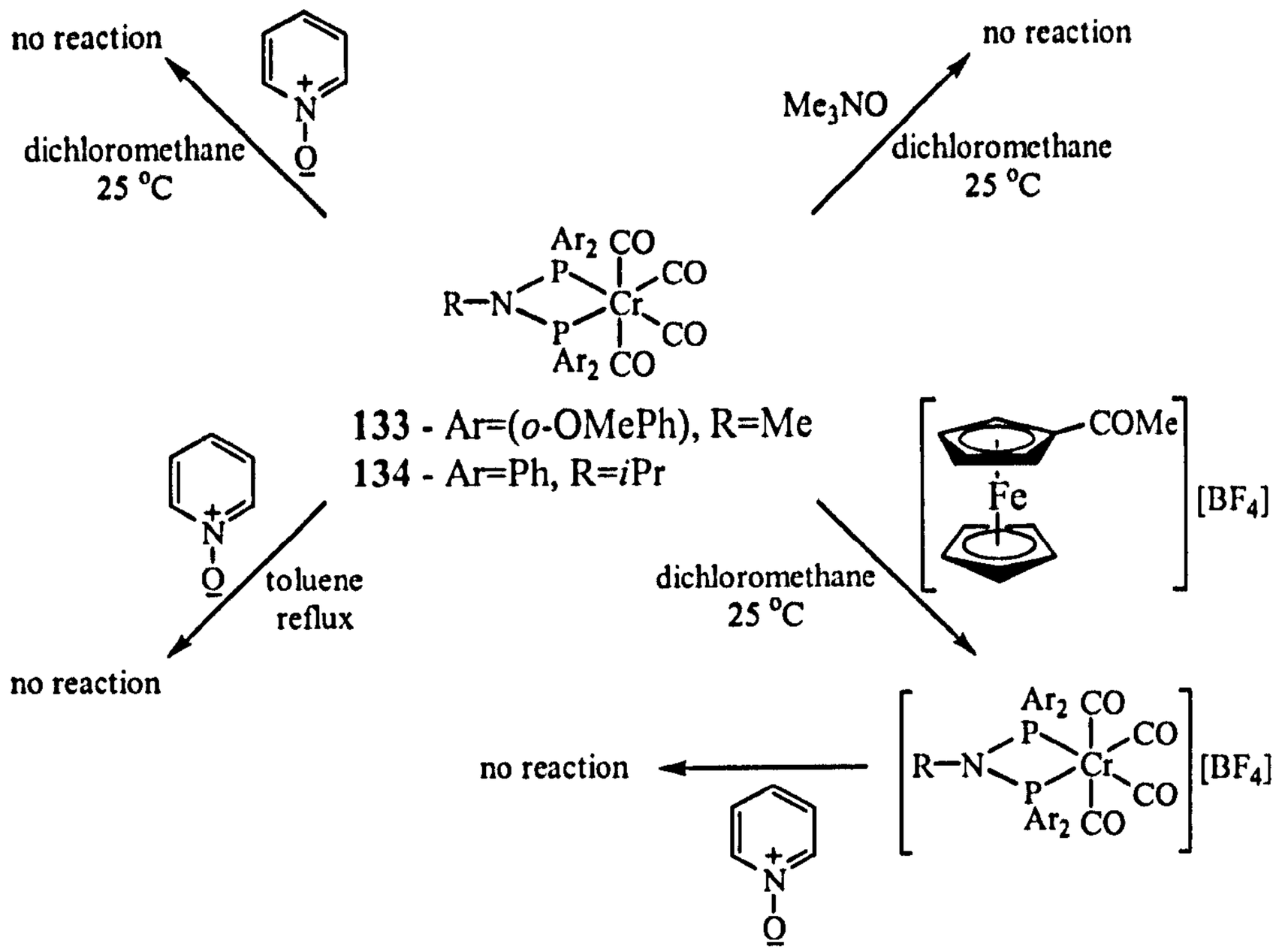
The use of this method with chromium carbonyl complexes also known where trimethylamine-N-oxide is added to a mixture of $[Cr(CO)_6]$ and dppm, to assist in the formation of $[Cr(CO)_4(dppm)]$.[153]

Removal of the CO ligand occurs *via* oxidation to CO_2, Scheme 4.13 shows how this occurs.[158]



Scheme 4.13 – Removal of CO Ligands

The first compounds tested for removal of CO ligands were trimethylamine-N-oxide (TMNO) and pyridine-N-oxide (PyNO). The attempted reactions are shown in Scheme 4.14.[158]

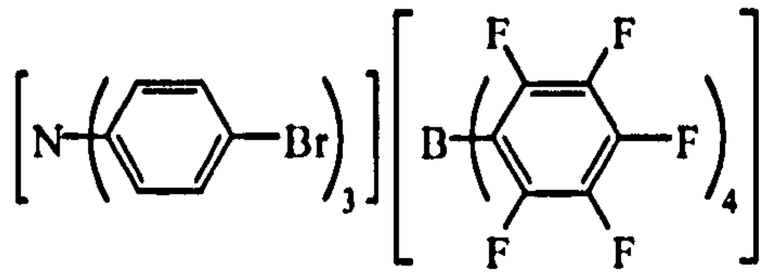


Scheme 4.14 – Removal of Carbonyl Ligands with PyNO or TMNO

It can be seen from Scheme 4.14 that the removal of CO ligands using TMNO or PyNO was unsuccessful. As stated in Section 4.1.1, Balakrishna and co-workers found that the addition of TMNO to $[Cr(CO)_4(PNP)]$ complexes in the presence of free ligand, did not lead to further CO replacement.[145] Therefore it is not surprising that this method of CO removal was unsuccessful.

4.4.3. Oxidation using an Oxidising Agent with a Weakly Coordinating Anion

McGuinness and co-workers showed that using chromium PNP systems with $Ag[Al(OC(CF_3)_3)_4]$ as the cocatalyst and $AlEt_3$ as an alkylating agent gave an active trimerisation catalyst.[52] Therefore we hypothesised that using an oxidising agent with a large weakly coordinating anion may result in a more active catalyst. The oxidising agent chosen was $[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$, **142** (Figure 4.7), with a weakly coordinating $[B(C_6F_5)_4]^-$ anion. $[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$ was chosen as the compound was available in the department and was donated by Neil Connelly and group.



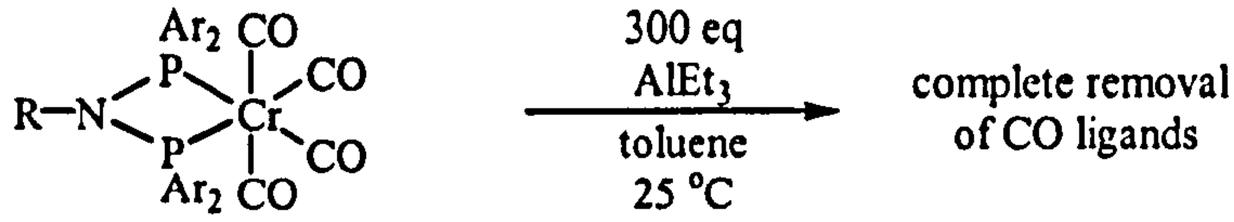
142

Figure 4.7 - $[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$

Due to the small quantity of the compound available, no *in situ* reactions were completed, the system was directly tested for ethene trimerisation at high pressure, see Section 4.5.3.

4.4.4. Attempted *In Situ* Reactions for Removing CO from Chromium Carbonyl Complexes using Alkyl Aluminium Compounds

The Tosoh Corporation reported a number of Cr(0) tricarbonyl based systems, with a wide range of ligands.[159] Triisobutyl aluminium ($Al(iBu)_3$) was used as the cocatalyst and the catalysts were activated by irradiation with UV light, suggesting that $Al(iBu)_3$ is used to remove CO ligands. Therefore the use of an alkyl aluminium compound, $AlEt_3$, as a CO scavenger was investigated. A series of *in situ* reactions were completed, where $AlEt_3$ was reacted with complexes **133** and **134**, as shown in Scheme 4.15.



133 - Ar=(*o*-OMePh), R=Me

134 - Ar=Ph, R=*i*Pr

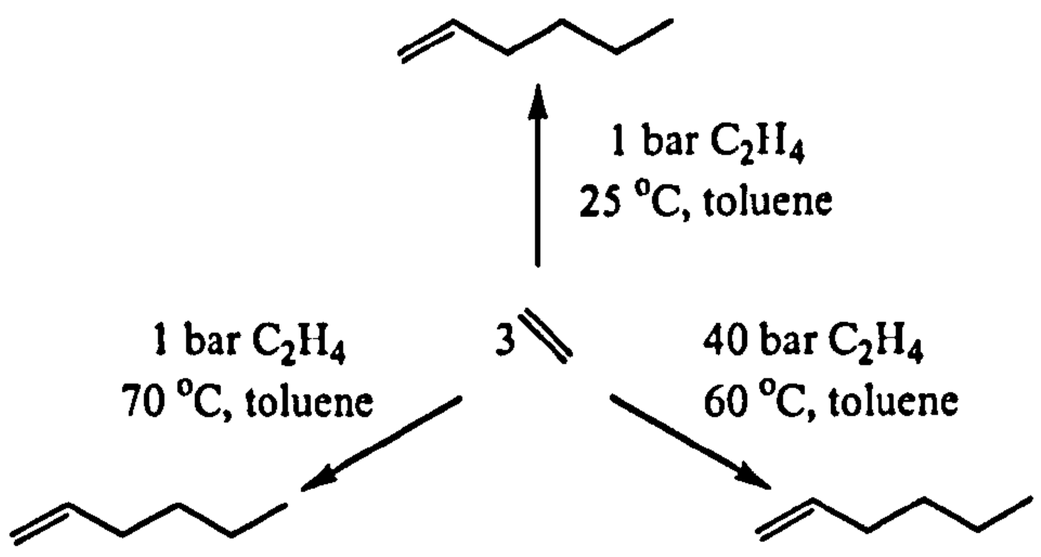
Scheme 4.15 – Removal of CO Ligands with $AlEt_3$

A toluene solution of $AlEt_3$ was added to a toluene solution of the carbonyl complex and the reaction was monitored by IR spectroscopy. After 15 mins the IR spectrum of the reaction showed that all four CO ligands had been removed. The product was not

isolated and the species formed is unknown. It is not known how $AlEt_3$ abstracts the CO ligands, although $AlEt_3$ may acts as an alkylating agent or as a Lewis acid.

4.5. Ethene Trimerisation with Chromium Carbonyl Complexes

Complexes **133, 134, 135** and **136** were tested for ethene trimerisation. Various catalytic systems were tested involving acetyl ferrocinium tetrafluoroborate, $[AcFe][BF_4]$ as the oxidant. Three sets of conditions were investigated as shown in Scheme 4.16.

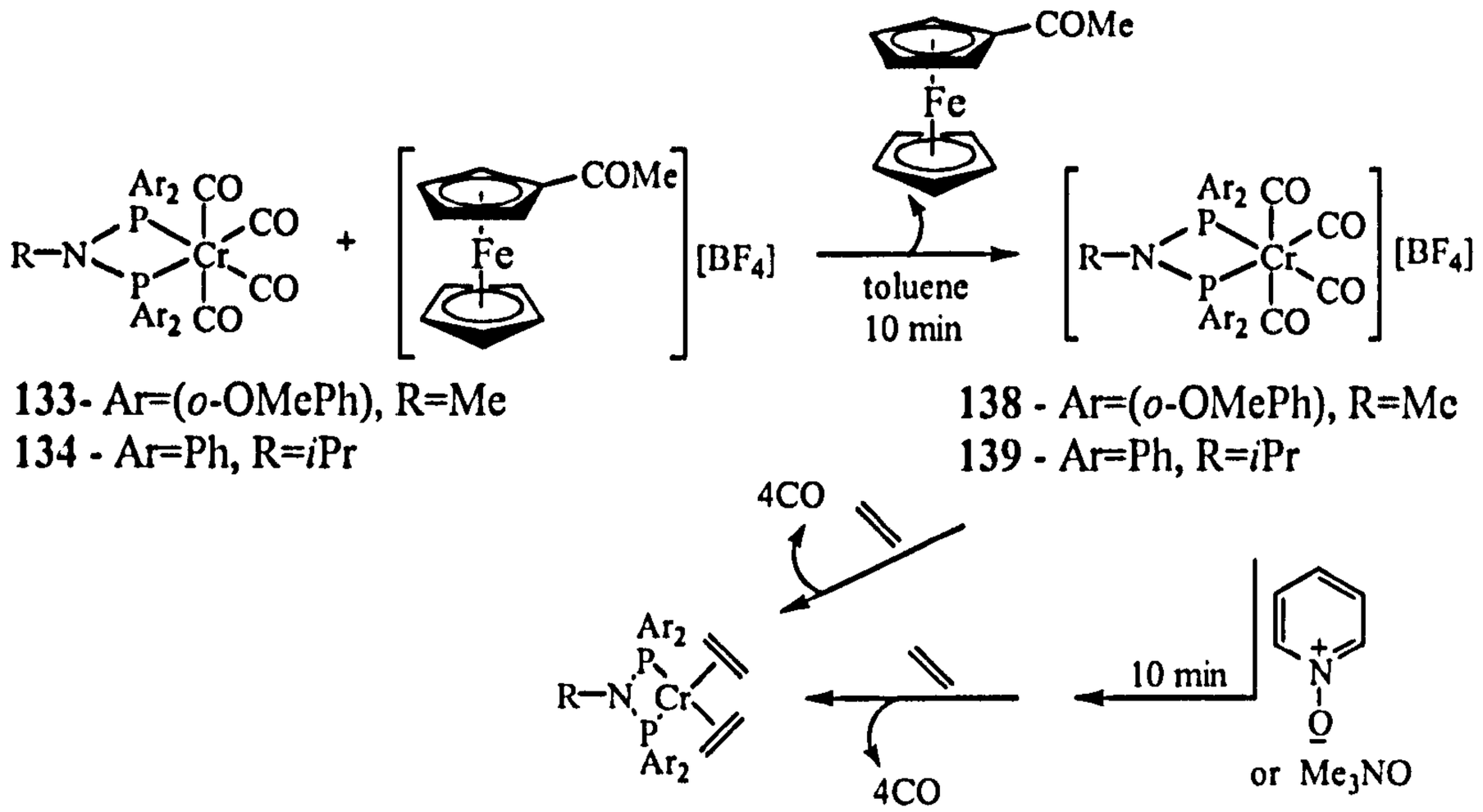


Scheme 4.16 – Reaction Conditions for Ethene Trimerisation

The reaction conditions are: 1 bar of ethene at 25 °C or 1 bar of ethene at 70 °C. High pressure ethene catalytic tests were conducted in a multi-cell autoclave under 40 bar of ethene at 60 °C. Each of the following reaction schemes (Scheme 4.17 to Scheme 4.19) were tested using each of the reaction condition shown in Scheme 4.16.

4.5.1. Ethene Trimerisation using $[AcFe][BF_4]$ as Oxidant, with Amine Oxides

The method tested is shown in Scheme 4.17, with the catalyst system and the reaction conditions used. $[Cr(CO)_4(\mathbf{1})]$ and $[Cr(CO)_4(\mathbf{19})]$ were used as the chromium precursors. The chromium carbonyl precursor was stirred with $[AcFe][BF_4]$ in dichloromethane for 10 minutes to oxidise the chromium centre. Next the solution was placed under ethene and stirred for three hours. In each case 0.5 mmol of $[Cr(CO)_4(PNP)]$ was used with 1.2 equivalents of the oxidant, $[AcFe][BF_4]$ and toluene was used as the solvent.



133- Ar=(*o*-OMePh), R=Me
134 - Ar=Ph, R=*i*Pr

138 - Ar=(*o*-OMePh), R=Me
139 - Ar=Ph, R=*i*Pr

Scheme 4.17 – Ethene Trimerisation Using [Cr(CO)$_4$(PNP)], [AcFe][BF$_4$] and Amine Oxides.

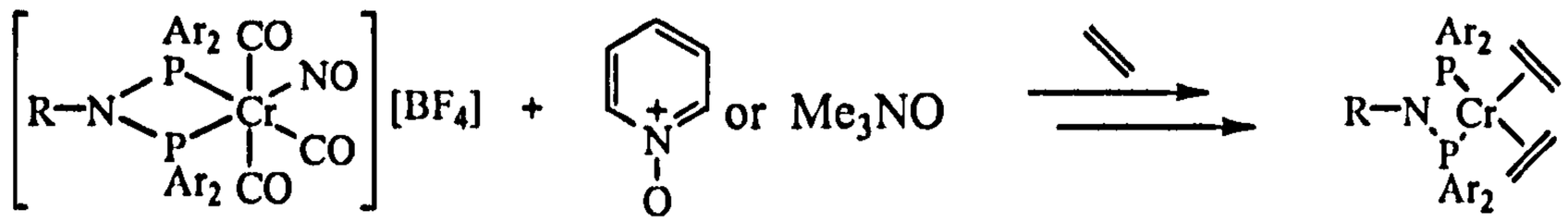
The production of hexene was not observed for this system using only the chromium precursor and [AcFe][BF_4].

To use chromium carbonyl PNP complexes for ethene trimerisation, removal of the CO ligands is needed so that a vacant site is available for ethene coordination. It was hypothesised that under the conditions shown in Scheme 4.17, this was not occurring. Therefore TMNO or PyNO were added to the system to remove CO ligands, although this had little effect on the activity of the system, which is not surprising given the results observed in Section 4.4.2. The production of hexene was not observed at either 1 bar at room temperature or 40 bar of ethene at 60 °C. This suggests that, as with the *in situ* reactions (Section 4.4.2), the addition of TMNO or PyNO does not promote the removal of CO ligands from the chromium centre to allow trimerisation to occur.

4.5.2. Ethene Trimerisation using Chromium Carbonyl Nitrosyl Complexes

[Cr(CO)$_3$(NO)(**1**)][BF_4], **136** and [Cr(CO)$_3$(NO)(**19**)][BF_4], **137** were synthesised by reacting [Cr(CO)$_4$(**1**)] and [Cr(CO)$_4$(**19**)] with [NO][BF_4], as reported in Section 4.3.4. It was hypothesised that the presence of the NO^+ ligand decreases the electron density around the metal centre. This in turn will decrease the back-bonding from metal centre

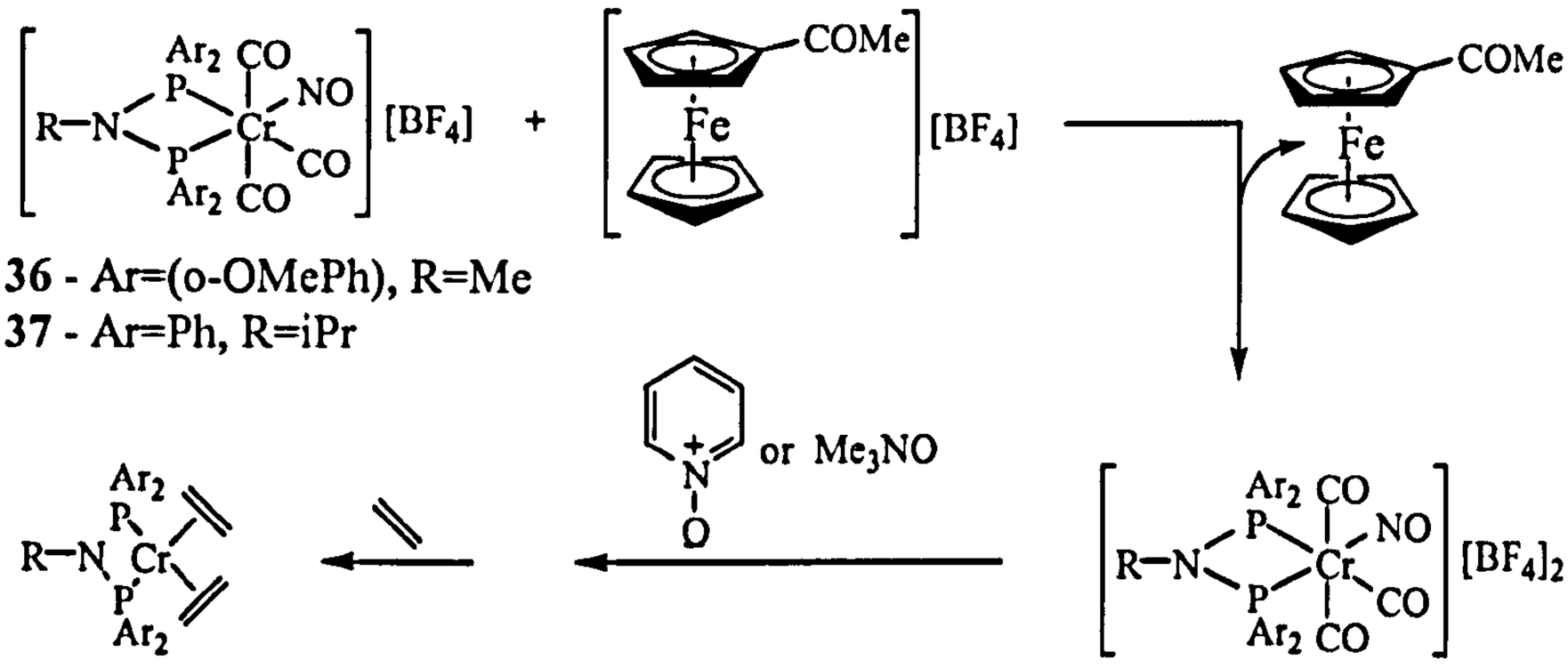
to the carbonyl ligands and decrease the strength of the metal-carbonyl bonds. The reaction schemes tested are shown in Scheme 4.18.



136 - Ar=(o-OMePh), R=Me
137 - Ar=Ph, R=iPr

Scheme 4.18 – Reaction of [Cr(CO)$_3$(NO)(1)][BF$_4$] and [Cr(CO)$_3$(NO)(19)][BF$_4$] with TMNO or PyNO

As shown in Scheme 4.18, complexes **136** and **137** were reacted with TMNO or PyNO and then the reaction vessel was placed under ethene. Again no hexene was observed.



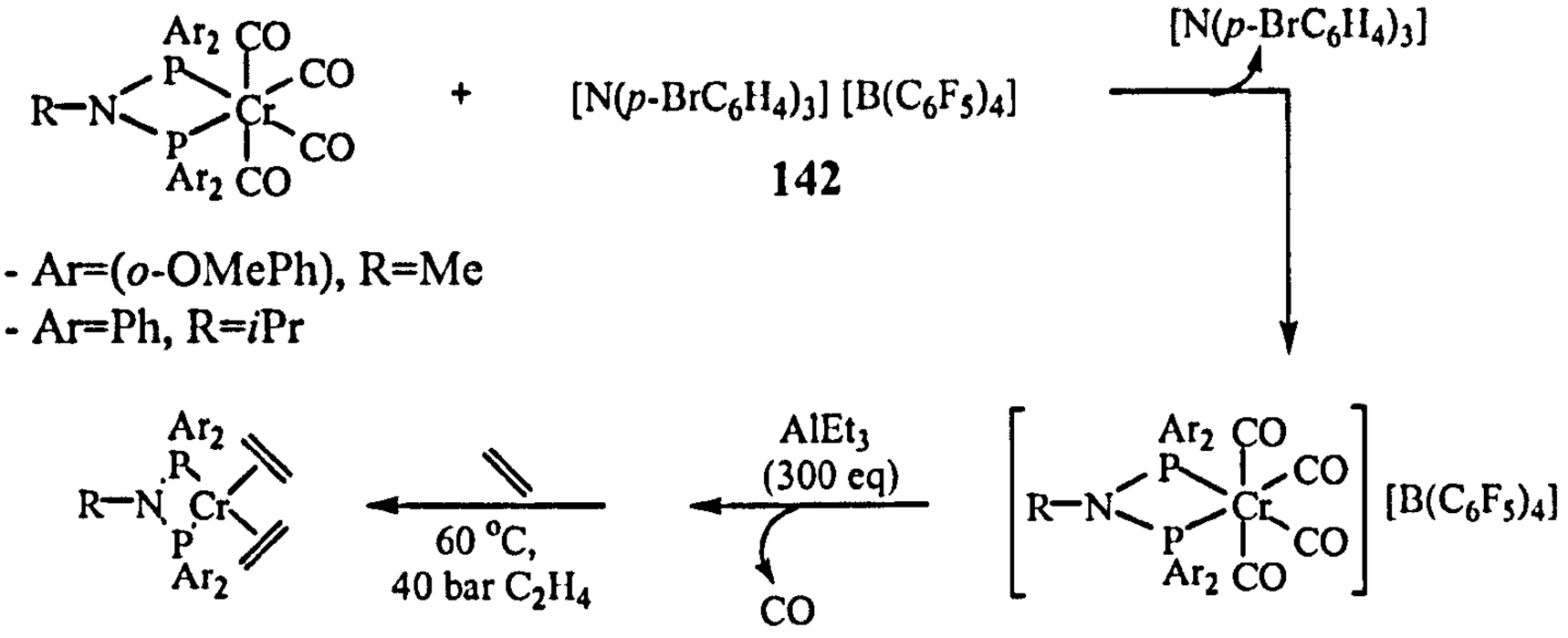
136 - Ar=(o-OMePh), R=Me
137 - Ar=Ph, R=iPr

Scheme 4.19 – System Using [Cr(CO)$_3$(NO)(PNP)] With [AcFe][BF$_4$]

In Scheme 4.19 complexes **136** and **137** were reacted with [AcFe][BF$_4$] and TMNO or PyNO and placed under ethene. As with the reaction in Scheme 4.10, there was no evidence of the formation of hexene.

4.5.3. Ethene Trimerisation using Oxidant with Weakly Coordinating Anion and $AlEt_3$

It was hypothesised that an oxidant was needed with a large weakly coordinating anion (see Section 4.4.3). The reaction scheme followed is shown in Scheme 4.20.[160]



Scheme 4.20 – Catalytic System with $[Cr(CO)_4(PNP)]$, $[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$. 142 and $AlEt_3$

In Scheme 4.20 $AlEt_3$ is used as a CO scavenger to remove CO ligands from the chromium carbonyl complexes, as shown in Section 4.4.2.

The experimental procedure for the trimerisation/tetramerisation of ethene with the system shown in Scheme 4.20 is as follows. First the chromium carbonyl PNP complex was oxidised by $[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$ to give $[Cr(CO)_4(PNP)][B(C_6F_5)_4]$. Next 300 molar equivalents of $AlEt_3$ in toluene was added to remove the CO ligands from $[Cr(CO)_4(PNP)][B(C_6F_5)_4]$. Finally the reaction was heated to 60 °C and placed under 40 bar of ethene. The products were analysed by GC and compared to an internal mesitylene standard. The number of moles and volumes of reaction components are 5 μmol $[Cr(CO)_4(PNP)]$, 5 μmol of oxidant, 1.5 mmol of $AlEt_3$ (1.9 M in toluene) and 4 mL of toluene.

Table 4.8, runs 4.1 to 4.4 shows that results obtained from ethene trimerisation/tetramerisation using a catalytic system with $[Cr(CO)_4(PNP)]$,

$[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$ and $AlEt_3$. The GC trace showed that α-alkenes were present in the reaction mixture.

Table 4.8 – Results from Catalytic System with $[Cr(CO)_4(PNP)]$, Oxidant and $AlEt_3$

Run	Chromium Precursor	Oxidising Agent	Productivity / g (g Cr h)$^{-1}$	Product Distribution / %	
				C_6	C_8
4.1	$[Cr(CO)_4$**(1)**$]$	$[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$	710	80	20
4.2	$[Cr(CO)_4$**(19)**$]$	$[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$	210	>99	-
4.3	$[Cr(CO)_4$**(5)**$]$	$[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$	0	-	-
4.4	$[Cr(CO)_4$**(1)**$]$	None	0	-	-
4.5[a]	$[Cr(CO)_4$**(1)**$]$	$[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$	0	-	-

[a] no $AlEt_3$ added

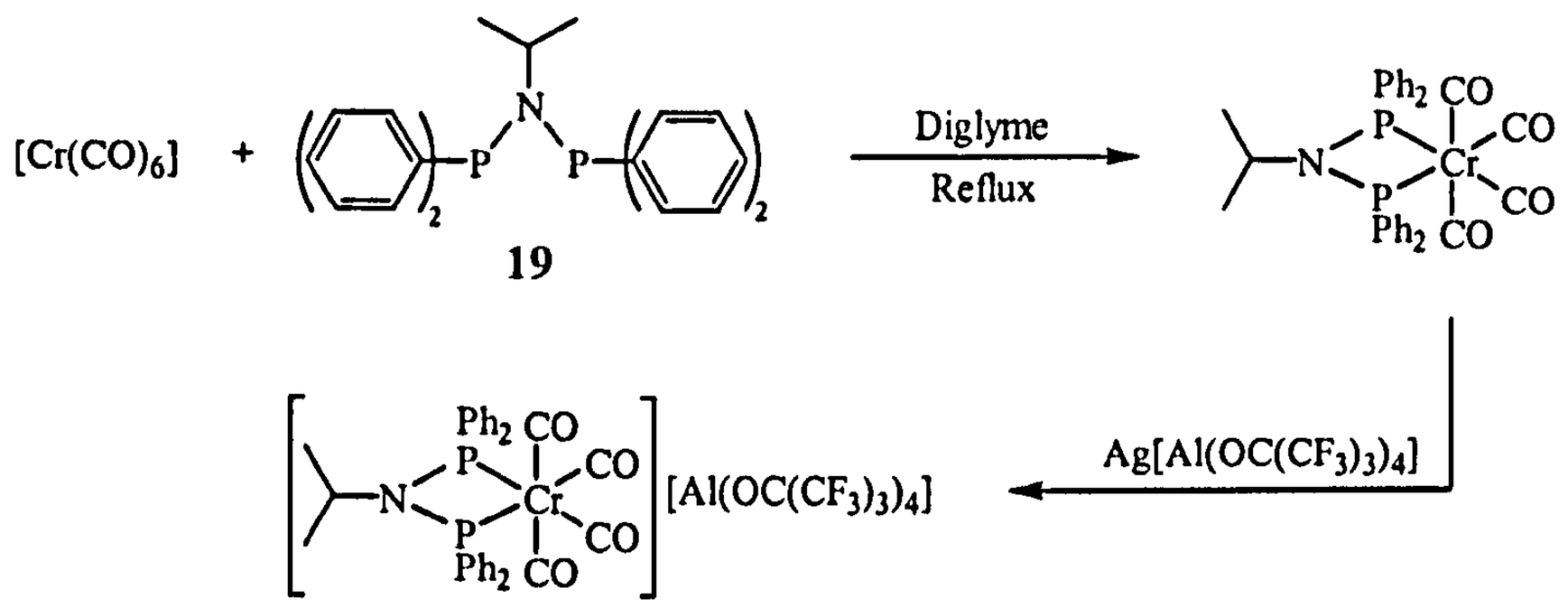
The highest productivity came from run 4.1, with a productivity of 710 g (g Cr h)$^{-1}$, using $[Cr(CO)_4$**(1)**$]$, this system showed a selectivity to hexene of 80 % and to octene of 20 %. Whereas the same system using $[Cr(CO)_4$**(19)**$]$ (run 4.2) gave a selectivity to hexene of over 99 % but only gave a productivity of 210 g (g Cr h)$^{-1}$. Due to the low productivities of the catalysts shown in Table 4.8, the selectivity towards 1-hexene and 1-octene could not be obtained. It is not possible to give accurate selectivity results due to the octene peak coinciding with the solvent peak on the GC trace.

In run 4.3 the system using $[Cr(CO)_4$**(5)**$]$ was found to be inactive towards ethene trimerisation. Run 4.4 shows that no hexene or octene is formed if the oxidising agent in not present, supporting the theory that the active catalyst has a Cr(I) centre and trimerisation does not occur if the metal centre is not oxidised from Cr(0) to Cr(I). Run 4.5 shows that no hexene is produced if $AlEt_3$ is not present.

4.5.4. Comparison with Work Published During This Investigation

4.5.4.1. Results Published by McGuinness and Co-worker

During the course of our studies, a similar approach was independently described by McGuinness and co-workers, their results being published shortly after ours.[155] The group investigated a selection of Cr(0) carbonyl PNP complexes. One of the systems developed by McGuinness and co-workers is shown in Scheme 4.21.



Scheme 4.21 – Synthesis of [Cr(CO)$_4$(19)][Al(OC(CF$_3$)$_3$)$_4$

[Cr(CO)$_4$(**19**)] was synthesised by reacting [Cr(CO)$_6$] with ligand **19**. This was then reacted with Ag[Al(OC(CF$_3$)$_3$)$_4$], to give [Cr(CO)$_4$(**19**)][Al(OC(CF$_3$)$_3$)$_4$], which was isolated as a purple solid. The reaction of [Cr(CO)$_4$(dppm)] with Ag[Al(OC(CF$_3$)$_3$)$_4$] does not give [Cr(CO)$_4$(dppm)][Al(OC(CF$_3$)$_3$)$_4$], but another unidentified product. It is suggested that the formation of another product or the fast decomposition of [Cr(CO)$_4$(dppm)][Al(OC(CF$_3$)$_3$)$_4$] is due to either the acidic methyl protons on the backbone of dppm or cleavage of the P-C bond. [Cr(CO)$_4$(**19**)][BF$_4$] and [Cr(CO)$_4$(**19**)][PF$_6$] were also synthesised for comparison with [Cr(CO)$_4$(**19**)] [Al(OC(CF$_3$)$_3$)$_4$] when used for ethene tetramerisation.

The group previously suggested that both an alkylating and alkyl abstracting agent is needed for trimerisation or tetramerisation to occur, when using Cr(III) catalyst precursors. This is not the case for the Cr(I) carbonyl route, although a method is needed to remove CO ligands so that a vacant site is left for ethene coordination. Three

methods of CO removal are: by UV photolysis, *via* a reaction with AlR_3 and by a reaction with TMNO. It was found that in *in situ* reactions, the addition of AlR_3 to $[Cr(CO)_4(19)]$ or exposure to UV light, the removal of CO ligands was observed by IR spectroscopy, although photolysis did not results in complete CO ligand removal. The reaction of TMNO with $[Cr(CO)_4(19)]$ resulted in no loss of CO ligands. Therefore the addition of $AlEt_3$ and exposure to UV light were examined with respect to tetramerisation. A selection of results from the tetramerisation of ethene is shown in Table 4.9.

Table 4.9 – Ethene Tetramerisation with Cr(I) Carbonyl Catalysts

Run	Catalyst	AlR_3 (Equiv)	Prod.[a]	Product Distribution				
				C_6	1-C_6[b]	C_8	1-C_8[c]	PE
4.6	$[Cr(CO)_4(19)][57]$	$AlEt_3$ (200)	139,800	21.4	78.1	72.4	99.0	1.1
4.7	$[Cr(CO)_4(19)][57]$	$Al\textit{i}Bu_3$ (400)	28,400	21.2	79.0	72.7	99.0	2.4
4.8	$[Cr(CO)_4(19)][BF_4]$	$AlEt_3$ (400)	0	-	-	-	-	-
4.9	$[Cr(CO)_4(19)][PF_6]$	$AlEt_3$ (400)	0	-	-	-	-	-
4.10	$[Cr(CO)_4(19)]$	$AlEt_3$ (100)	1,600	15.5	65.1	20.6	35.4	59.4
4.11	$[Cr(CO)_4(dppe)]$ $[Al(OC(CF_3)_3)_4]$	$AlEt_3$ (200)	6,000	24.2	51.8	46.7	100.0	10.4
4.12[d]	$[Cr(CO)_4(19)]$ $[Al(OC(CF_3)_3)_4]$	-	0	-	-	-	-	-
4.13[d]	$[Cr(CO)_4(19)]$ $[Al(OC(CF_3)_3)_4]$	$AlEt_3$ (400)	85,000	21.4	76.9	71.6	98.7	1.2

0.05 mmol Cr Catalyst, 10 mL toluene, 90 mL methylcyclohexane, 60 °C, 40 bar ethene, 1 h; [a] productivity / g (g Cr h); [b] selectivity within C_6 fraction; [c] selectivity within C_8 fraction; [d] under photolysis for 10 min.

The system with the best results is in run 4.6, using $[Cr(CO)_4(19)][Al(OC(CF_3)_3)_4]$ and 200 equivalents of $AlEt_3$. A productivity of 139,800 g (g Cr h)$^{-1}$ was obtained with a selectivity to hexene of 21.4 % (78.1 % to 1-C_6) and to C_8 of 72.4 % (99.0 % to 1-C_8).

Using Al*i*Bu$_3$ (run 4.7) resulted in a lower productivity than AlEt$_3$, although selectivity was unchanged. Run 4.12, using photolysis and no AlEt$_3$ resulted in an inactive catalyst, although the combination of AlEt$_3$ and photolysis gave a productivity of 85,000 g (g Cr h)$^{-1}$ (run 4.13).

[Cr(CO)$_4$(**19**)][BF$_4$] (run 4.8) and [Cr(CO)$_4$(**19**)][PF$_6$] (run 4.9) were found to be inactive, this may be because the BF$_4$ and PF$_6$ counteranions are too strongly coordinating. [Cr(CO)$_4$(**19**)] (run 4.10) was found to be slightly active when activated with AlEt$_3$, although the selectivity towards polyethylene increases to 59.4 %. [Cr(CO)$_4$(**19**)][**57**] and AlEt$_3$ gave a productivity of 6,000 g (g Cr h)$^{-1}$, with a selectivity to C$_6$ of 24.2 % (51.8 % to 1-C$_6$) and 71.6 % to C$_8$ (98.7 % to 1-C$_8$). It was found that the amount of AlEt$_3$ added affected the productivity with 200 equivalents giving the highest productivities.

4.5.4.2. Ethene Trimerisation Using Ag[Al(OC(CF$_3$)$_3$)$_4$] for Comparison with Work by McGuinness and Co-workers

To compare the results obtained in our investigation of chromium carbonyl complexes with the results obtained by McGuinness and co-workers, a series of ethene trimerisation tests were carried out using Ag[Al(OC(CF$_3$)$_3$)$_4$] as the oxidising agent.[155] The results obtained are shown in Table 4.10.

Table 4.10 – Results from Catalytic System with $[Cr(CO)_4(PNP)]$, $Ag[Al(OC(CF_3)_3)_4]$ and $AlEt_3$

Run	Chromium Precursor	Oxidising Agent	Productivity / g (g Cr h)$^{-1}$	Product Distribution / %	
				C_6	C_8
4.14	$[Cr(CO)_4$**(1)**$]$	$Ag[Al(OC(CF_3)_3)_4]$	210	> 99	0
4.15	$[Cr(CO)_4$**(19)**$]$	$Ag[Al(OC(CF_3)_3)_4]$	230	70	30
4.16	$[Cr(CO)_4$**(5)**$]$	$Ag[Al(OC(CF_3)_3)_4]$	0	-	-
4.17[a]	$[Cr(CO)_4$**(1)**$]$	$Ag[Al(OC(CF_3)_3)_4]$	110	-	-
4.18	$[Cr(CO)_4$**(1)**$]$	None	0	-	-

[a] cyclohexane used as the solvent

Table 4.9 shows that results obtained from ethene trimerisation/tetramerisation using a catalytic system with $[Cr(CO)_4(PNP)]$, $Ag[Al(OC(CF_3)_3)_4]$ and $AlEt_3$. As with the system using $[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$ in Table 4.9, the production of 1-hexene was observed, although the productivities are lower than for $[N(p\text{-}BrC_6H_4)_3][B(C_6F_5)_4]$ for the $[Cr(CO)_4$**(1)**$]$ system. The best results came from run 4.15, with a productivity of 230 g (g Cr h)$^{-1}$, using $[Cr(CO)_4$**(19)**$]$, this system showed a selectivity to hexene of 70 % and to octene of 30 %. Whereas the same system using $[Cr(CO)_4$**(1)**$]$ (run 4.14) gave a selectivity to hexene of over 99 % but only gave a productivity of 210 g (g Cr h)$^{-1}$. In run 4.16 the system using $[Cr(CO)_4$**(5)**$]$ was found to be inactive towards ethene trimerisation. Run 4.17 shows that no hexene or octene is formed if the oxidising agent in not present, supporting the theory that the active catalyst has a Cr(I) centre and trimerisation does not occur if the metal centre is not oxidised from Cr(0) to Cr(I). Run 4.4 shows that no hexene is produced if $AlEt_3$ is not present.

The productivities obtained by our systems are much lower than that obtained by McGuinness and co-workers. This may be due to differences in experimental technique or the grade of chemicals used.

4.6. Summary

A Cr(I)/Cr(III) mechanism has been proposed for the trimerisation of ethene.[6, 58] Bercaw and co-workers showed evidence for this mechanism by synthesising $[CrPh_3(thf)_3]$ and [CrBr(*o*,*o*'-biphenyldiyl)], **35**.[5, 40] McGuinness and co-workers investigated new activation systems which could be used as an alternative to MAO and found that system using aluminates along with $AlEt_3$ produced the best results.[52, 81] Systems using aluminates with weakly coordinating anions, such as $Ag[Al(OC(CF_3)_3)_4]$ showed high activities towards ethene tetramerisation and were stable over long periods.

A selection of results from this chapter has been published.[160] It was suggested that another route to the Cr(I) species is from Cr(0) complexes followed by oxidation to Cr(I). In this chapter the use of chromium(0) carbonyl PNP complexes for ethene trimerisation was investigated. Cr(0) complexes $[Cr(CO)_4(1)]$, **133**, $[Cr(CO)_4(19)]$, **134** and $[Cr(CO)_4(5)]$, **135**, were synthesised and the molecular structure of each complex is reported. Complexes **133**, **134** and **135** show an octahedral arrangement of ligands around the chromium centre. In comparing complexes **133** and **134**, it was suggested that ligand **1** is more basic than ligand **19**, this was supported by the IR data of the two complexes. Complex **135** showed similar IR stretching frequencies, bond lengths and angle to complex **133**, showing that the nitrogen in the backbone of **19** or **1** does not have a large impact on the bonding. The molecular structure and IR spectrum of $[Cr(CO)_3(NO)(1)]$, **136** showed that the presence of the NO ligand decreases the strength of the metal-carbonyl bond.

The oxidation of complexes **133**, **134** and **135** was investigated, where the cyclic voltammagram of each complex showed a reversible oxidation. Complexes **133**, **134** and **135** were reacted with acetyl ferrocinium tetrafluoroborate and were shown by IR spectroscopy to undergo oxidation. For chromium carbonyl PNP complexes to be used for ethene trimerisation, a method for removing the carbonyl ligands is needed. In this chapter TMNO or PyNO were tested and found to be inactive towards removing CO ligands, even at elevated temperatures.

A number of systems using complexes **133, 134** and **135** were tested for ethene trimerisation and it was found that an oxidising agent with a weakly coordinating anion is needed, along with a CO scavenger. Using [AcFe][BF_4] and TMNO or PyNO showed no evidence of hexene production. The best results were produced by a system using [$Cr(CO)_4$(**1**)], [$N(p\text{-}BrC_6H_4)_3$][$B(C_6F_5)_4$] and $AlEt_3$, giving a productivity of 710 g (g Cr h)$^{-1}$, at 45 °C and 45 bar of ethene.

Although the activity of chromium carbonyl PNP catalysts is lower than the Cr(III) analogues, the benefit of these systems is the low cost of $AlEt_3$ compared to MAO.

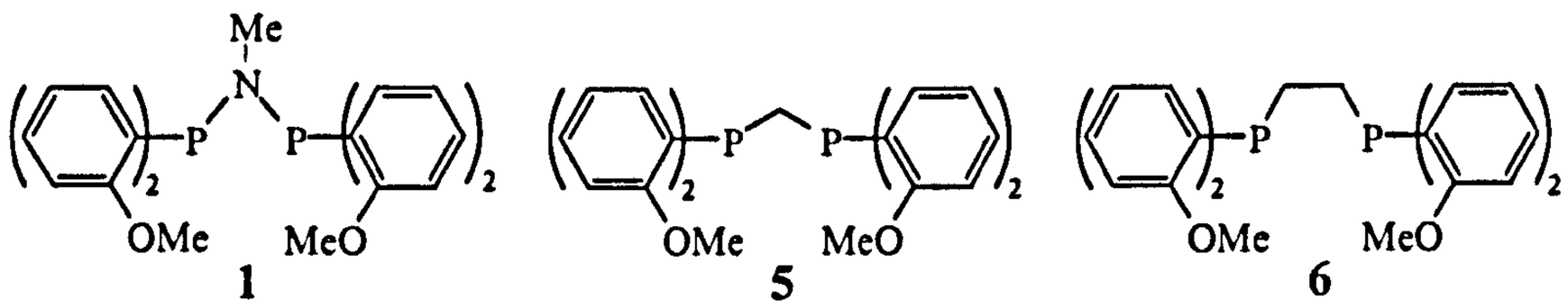
Chapter 5

Phosphine Ligands for Ethene Trimerisation

5.1. Introduction

5.1.1. Background to Phosphine Ligands for Ethene Oligomerisation

Chromium *N,N*-bis(diarylphosphino)alkylamine systems have been shown to be highly active towards ethene trimerisation and tetramerisation (in Section 1.2.1.3). One of the best systems to date was developed by Wass and co-workers, using $[CrCl(thf)_3]$, *N,N*-bis(di-*ortho*-methoxyphenylphosphino)methylamine, **1** and methylaluminoxane (MAO), Scheme 1.8, which was highly selective 1-hexene formation at low ethene pressures, with a productivity of 1,033,000 g (g Cr h)$^{-1}$ and an overall 1-C_6 selectivity of 89.9 %.[1,4] The equivalent bis(di-*ortho*-methoxyphenylphosphino)methane, **5**, and bis(di-*ortho*-methoxyphenylphosphino)ethane, **6**, ligands, shown in Figure 5.1, were also tested and found to be inactive for trimerisation at low ethene pressure.[1,4]

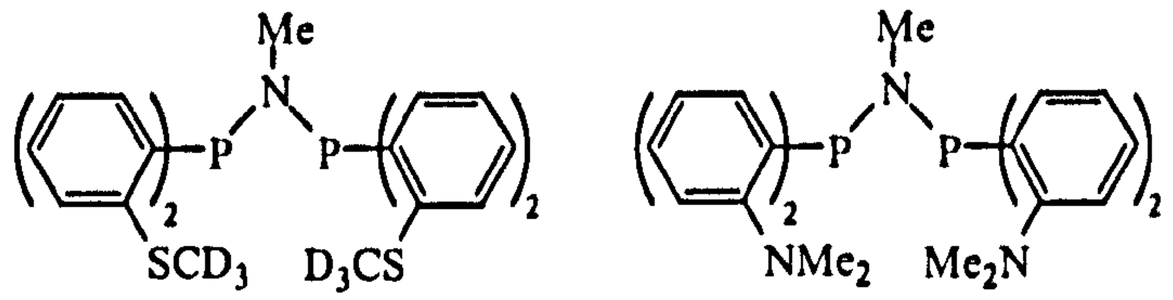


1 **5** **6**

Figure 5.1 – Bidentate Phosphine Ligands with Oxygen Donors

Bercaw and co-workers extended the work into ligand **1** and found that one of the OMe groups on the phenyl rings acted as a pendant ligand to the chromium centre, giving a six coordinate octahedral complex, the molecular structure is shown in Figure 1.2.[5] It is suggested that the unique ability of **1** ligand to become a tridentate system, stabilises the catalytic cycle and increases the selectivity towards the formation of 1-hexene.

The sulphur equivalent of **1** was investigated, where the OMe groups were replaced with SCD_3 groups, **8**. The molecular structure of $[CrPh_3(\mathbf{8})]$, **9**, is shown in Figure 1.5 showing that the ligand bonds *via* two sulphur atoms and one phosphorus from one side of the PNP ligand and not *via* the two phosphorus atoms. This was also shown to occur for ligand **143**, with NH_2 groups, where the ligands bond *via* two nitrogen atoms and one phosphorus.[36]

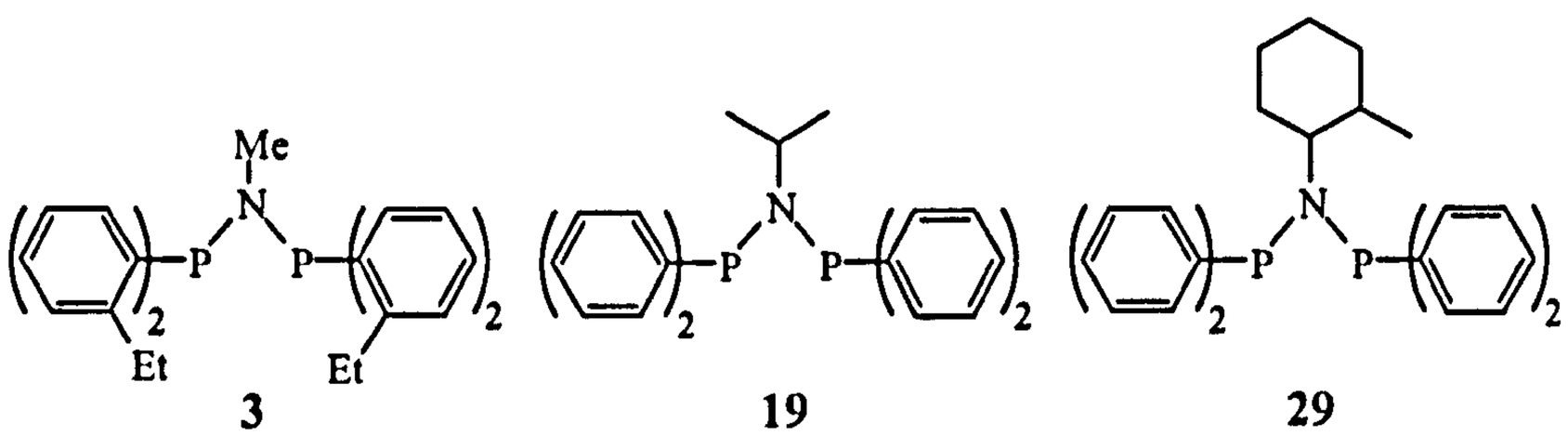


8 **143**

Figure 5.2 – Other PNP Ligands with Ortho Donor Groups

This shows that currently only the OMe group of **1** has been shown to act as a pendant donor the metal centre. Ligand **8** was not tested for ethene trimerisation and ligand **143** was found to be inactive.[36] A donor group is needed which does not preferentially bond to the metal centre over the two phosphorus atoms, but will act as a pendant ligand. This means that there is a fine balance between a group acting as a pendant ligand and bonding to metal centre over phosphorus. The possible route to developing new ligands is *via* more subtle changes to oxygen donor groups.

Bolmann and co-workers carried out extensive research on ethene trimerisation and tetramerisation on PNP ligands with various substituents on the nitrogen and phenyl groups.[41, 42, 47, 50,]



3 **19** **29**

Figure 5.3 – Ligands Tested by Bollmann and Co-workers

For ethene trimerisation, at 45 bar of ethene and 45 °C, **3** gave a productivity of 324,110 g (g Cr h)$^{-1}$, with a selectivity to C_6 of 90.7 %, of which 90.4 % is 1-C_6.[41] For ethene tetramerisation one of the best systems is [$CrCl_3(thf)_3$]/**19**/MAO.[42, 47] At 30 bar of ethene and 60 °C, this system gave a productivity of 272,400 g (g Cr h)$^{-1}$ and a selectivity of 68.3 % towards octene, of which 98.9 % is 1-octene. The system using **29** gave one of the highest productivities observed, of 2,279,200 g (g Cr h)$^{-1}$ at 45 bar of

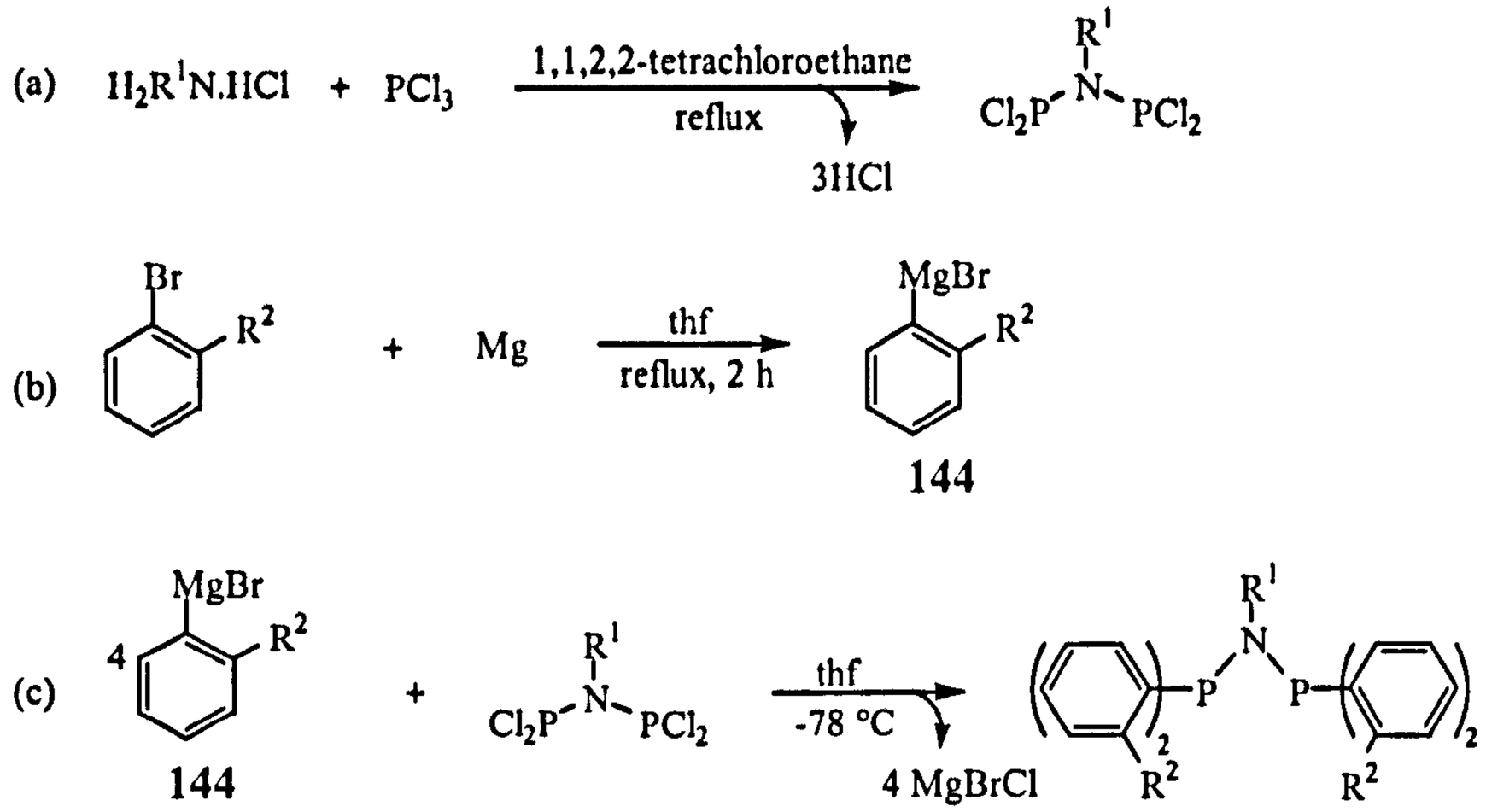
ethene and 60 °C, with a selectivity to C_8 of 63.7 %, of which 99.5 % is 1-C_8 (see reaction 1.47 in Table 1.14).[49]

The advantage of ligand **1** over the other ligands tested is that a high productivity and selectivity to 1-hexene is produced at 1 bar of ethene and room temperature. Therefore the aim of this chapter is to investigate PNP and dppe ligands with oxygen donor groups on the *ortho* position of the phenyl rings, with the aim to find other ligands that can trimerise ethene at 1 bar of ethene and room temperature.

5.1.2. Background to Ligand Synthesis

A range of methods for synthesising PNP ligands have been reported by Dossett and co-workers,[33] Cooley and co-workers,[34] Bollmann and co-workers[41, 42, 47] and Balakrishna and co-workers.[145]

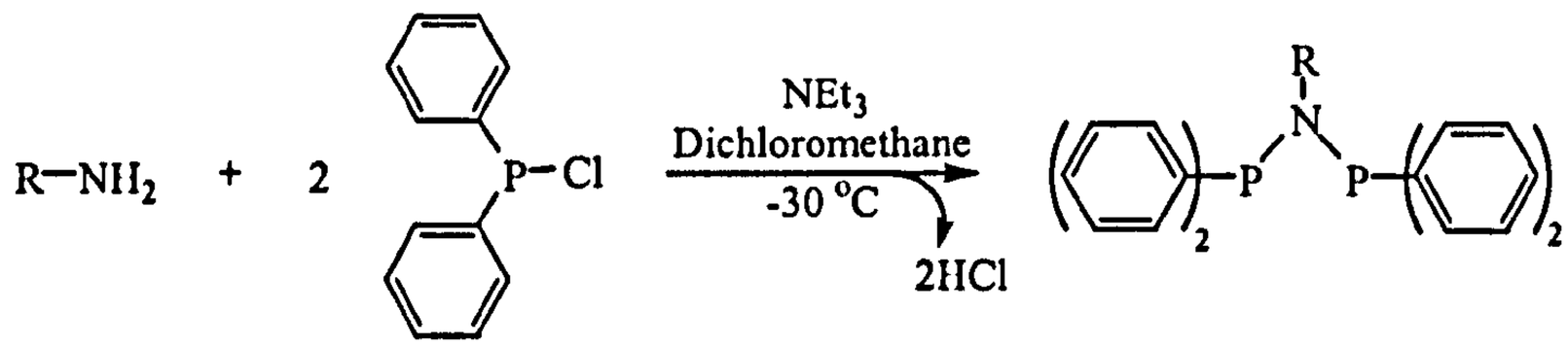
The first general method involves the formation of the PNP backbone by reacting phosphorus trichloride, PCl_3, with alkylamine hydrochloride salt, $H_2R^1N.HCl$ giving $Cl_2PN(R^1)PCl_2$, this involved refluxing the mixture in 1,1,2,2-tetrachloroethane at 150 °C for 7 days. The synthesis of $Cl_2PN(R)PCl_2$ compounds was reported by Nixon, where R is an alkyl group.[161, 162] In the next stage bis(dichlorophosphino)methylamine, $Cl_2PN(R^1)PCl_2$, is reacted with four equivalents of the arylmagnesium bromide, **144**, in tetrahydrofuran, to give the PNP ligand, shown as reaction (b) and (c) in Scheme 5.1. Scheme 5.1 shows the formation of PNP ligands with *ortho* substituents on the aryl groups, *para* and *meta* substituted aryl groups are also possible.



Scheme 5.1 – General Method 1 of Synthesis of PNP Ligands

This method is limited to forming PNP ligands with small substituents on the aryl groups. PNP ligands with large substituents, such as an isopropyl group, cannot generally be formed *via* this route as only one, two or three equivalents of the Grignard reagents will react with $Cl_2PN(R^1)PCl_2$ under reflux.

PNP ligands with unsubstituted phenyl rings are simpler to synthesise as diphenylphosphine chloride is commercially available. This method is shown in Scheme 5.2 and is classed as general method 2. This method was reported by Bollmann and co-workers.[41, 42, 47]

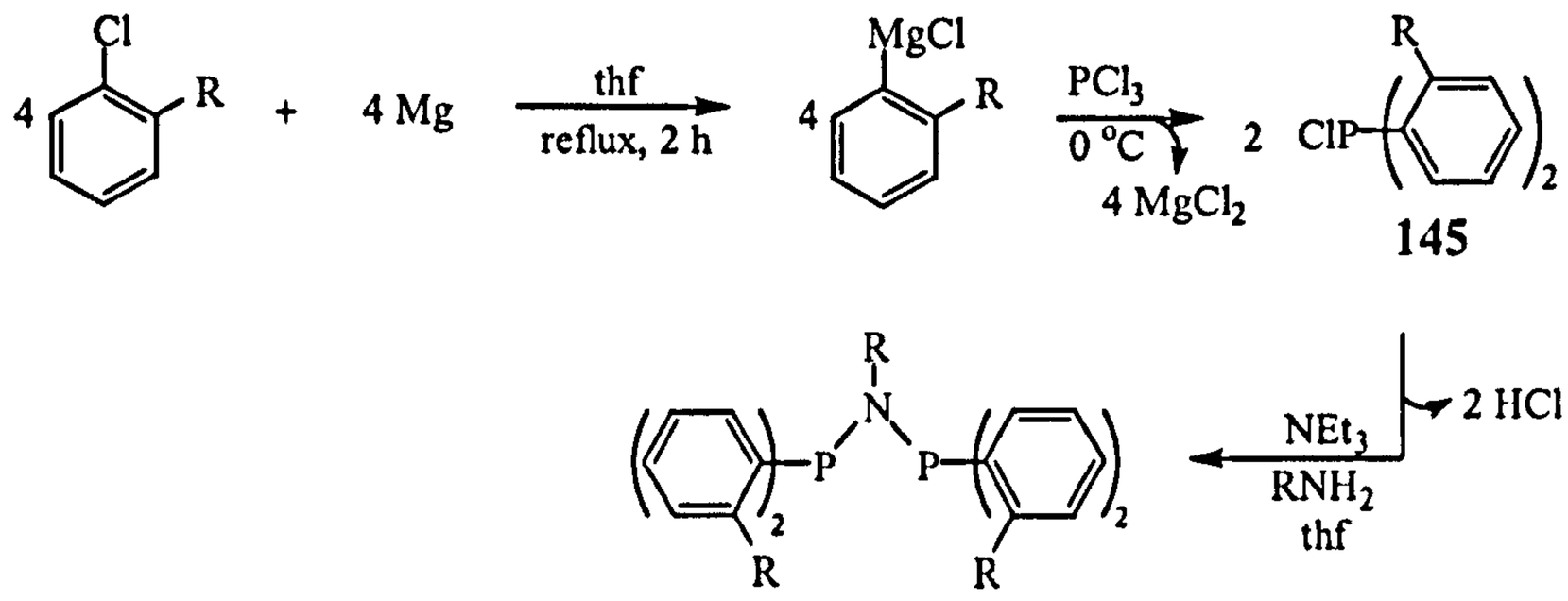


Scheme 5.2 – General Method 2 for Synthesis of PNP Ligands with Unsubstituted Phenyl Rings

In this method (Scheme 5.2) the primary amine is reacted with diphenylphosphine chloride, Ph_2PCl, in dichloromethane at -30 °C. The amine chosen depends on the

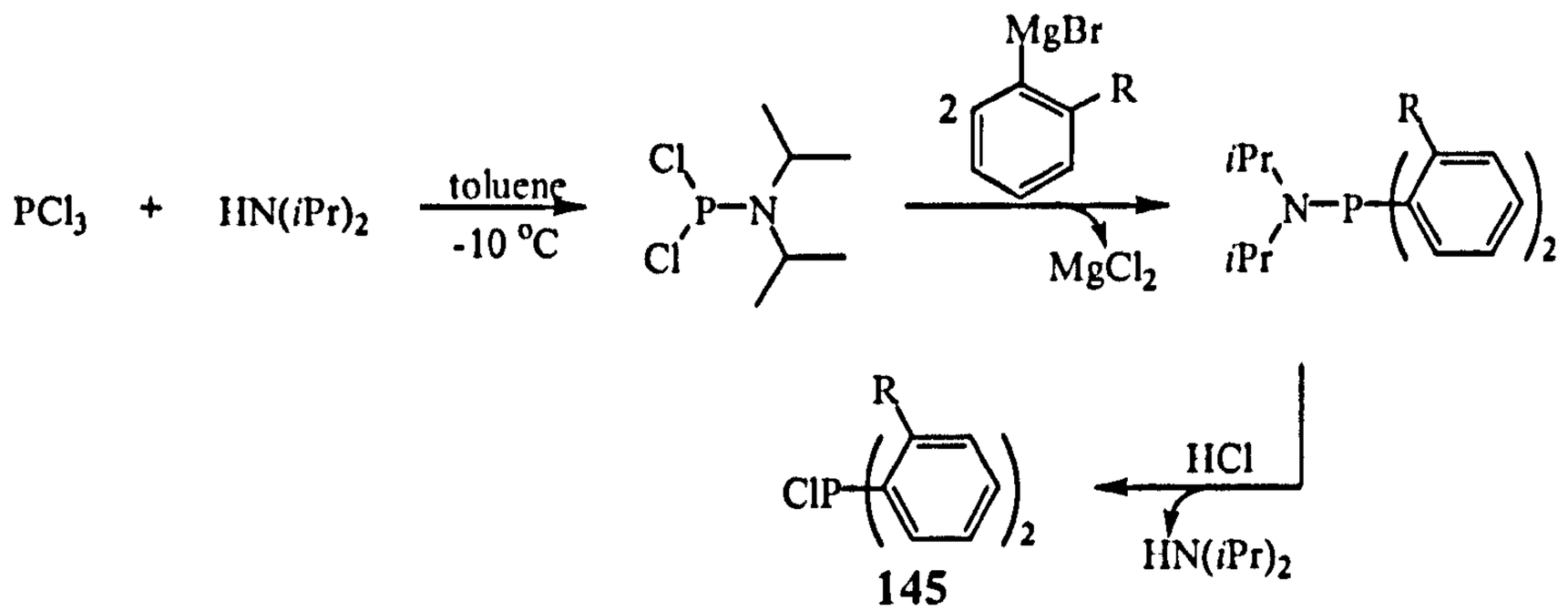
desired group on the nitrogen of the PNP ligand. Triethylamine is added in excess to promote abstraction of the proton from the amine and remove hydrochloric acid from the solution, giving triethylammonium chloride salt. This method is limited to PNP ligands with phenyl groups and cannot be used for PNP ligands with substituted aryl groups.

Bollmann and co-workers developed a series of methods for synthesising PNP ligands.[41, 42, 47] One method is shown in Scheme 5.3. This method was adapted from a method developed by Balakrishna and co-workers.[132] This method involves the reaction of PCl_3 with two equivalents of the Grignard reagent, arylmagnesium bromide to give a diarylphosphine chloride, **145**. Phosphorus tribromide can be used is place of PCl_3. This is followed by reacting two equivalents of the diaryl phosphine chloride, **145**, with a primary amine (see Scheme 5.3). As with method 2, triethylamine is added to abstract the proton from the primary amine and remove HCl from the solution.



Scheme 5.3 – General Method 3 for Synthesis of PNP Ligands

The problematic stage of this method is the formation of the diarylphosphine chloride, **16**, as the formation or triaryl phosphines is possible from the excess addition of the Grignard reagent. A modified version of this method of forming compound **145**, shown in Scheme 5.4, was reported by Rajan Babu and co-workers, where *N,N*-diisopropylphosphoramide dichloride, is first synthesised and reacted with the Grignard reagent instead of PCl_3, this reaction is more controlled as the formation of triaryl phosphines is prevented.[163]



145

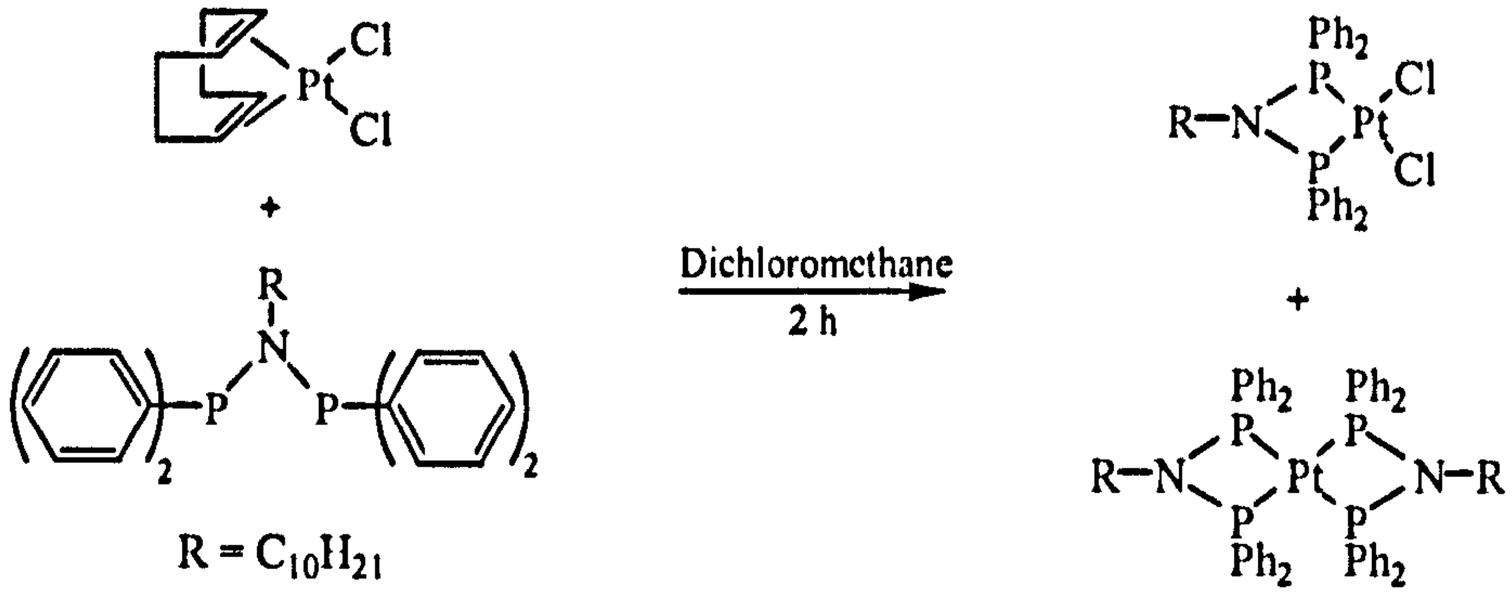
Scheme 5.4 – PNP Synthesis via N,N-diisopropylphosphoramide Dichloride

Firstly diisopropylamine is reacted with PCl_3 at -10 °C in toluene, as shown in Scheme 5.4. The resulting diisopropylphosphoramide dichloride, is then reacted with the Grignard reagent, followed by the addition of hydrochloric acid to give diarylphosphine chloride. This method can be used for PNP ligands with bulky substituents on the phenyl rings.

The method used to synthesise specific PNP ligands depends on the substituents and steric bulk of the desired PNP ligand.

5.1.3. Background to Chromium and Platinum Complex Synthesis

The synthesis of chromium carbonyl phosphine complexes is reported in Chapter 2. Platinum PNP complexes are known, Gallo and co-workers showed the synthesis of $[PtCl_2(PNP)]$ complexes with long chain alkyl groups on the nitrogen backbone, an example is given in Scheme 5.5. The complex was formed by reacting the ligand with $[PtCl_2(COD)]$ in dichloromethane.[164]



Scheme 5.5 – Synthesis of [$PtCl_2$(PNP)] complexes

It was found that along with [$PtCl_2$(PNP)], the formation of a bis-chelated species occurs, where two ligands coordinate to the metal centre. To prevent the formation of this species, a slow addition of the ligand to [$PtCl_2$(COD)] is needed. The ^{31}P NMR shifts given for the [$PtCl_2$(PNP)] complexes ranged from 17 ppm to 20 ppm, with phosphorus-platinum coupling constants of about 3300 Hz.[164]

5.2. Objectives

This chapter aims to investigate the synthesis of PNP and dppe ligands with *ortho* oxygen donor groups. These ligands are then coordinated to [$Cr(CO)_6$] or [$PtCl_2$(COD)]. The activity of the ligands for ethene trimerisation will be tested using [$CrCl_3(thf)_3$] and MAO as the activator.

5.3. Synthesis of Bidentate Phosphorus Ligands with Oxygen Donor Groups

5.3.1. Synthesis of *N,N*-Bis(diarylphosphino)methylamine (PNP) Ligands

The target PNP ligands are shown in Figure 5.4.

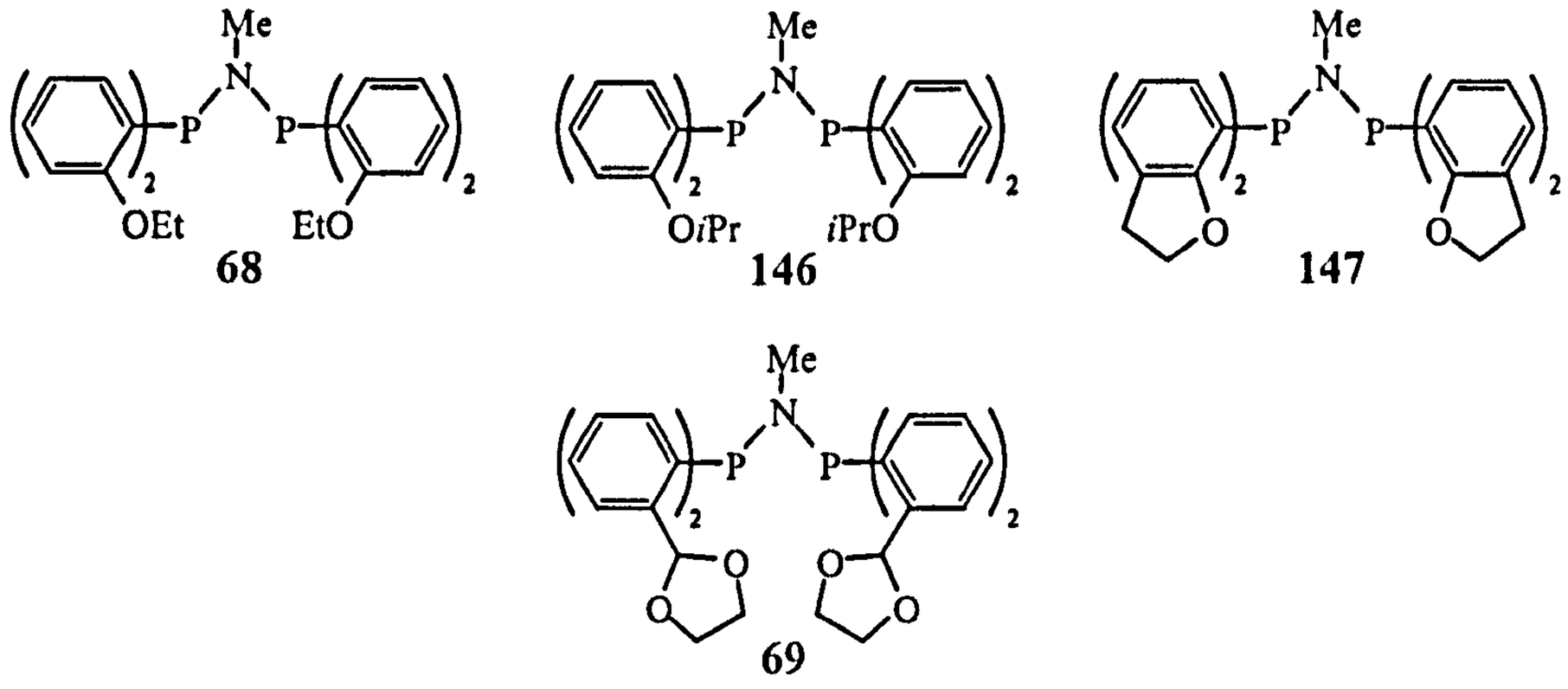
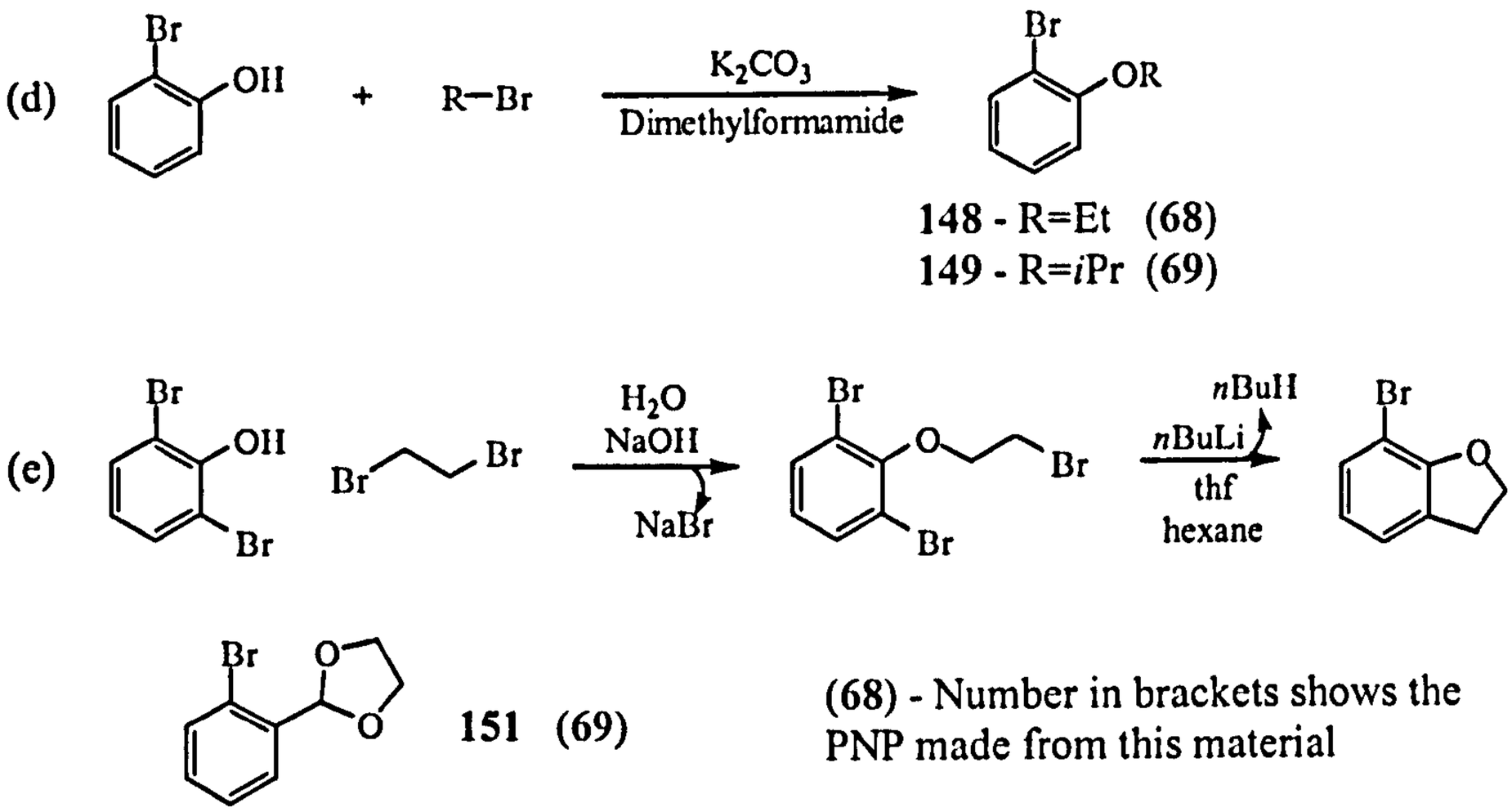


Figure 5.4 – Target PNP Ligands with Oxygen Donor Groups

N,N-bis(di-*ortho*-ethoxyphenylphosphino)methylamine **68** and *N,N*-bis(di-*ortho*-isopropoxyphenylphosphino)methylamine **146** contain alkoxy groups, which are similar to *N,N*-bis(di-*ortho*-methoxyphenylphosphino)methylamine **1**. The size of the alkoxy group is increased from an OMe group to an OEt in **146** and O*i*Pr group in **147**. This may prevent the oxygen binding to the metal centre and change to selectivity of the catalyst system when used in ethene trimerisation. *N,N*-bis(di(2,3-dihydrobenzofuran)-phosphino)methylamine **147** has dihydrobenzofuran groups attached to the phosphorus atoms, this forces the oxygen into one position with respect to the five membered ring. *N,N*-Bis-(di-*ortho*-(1,3-dioxolan-2-yl)phenyl)phosphino)methylamine **69** has dioxolane groups attached to the phenyl rings, this allows the possibility of either oxygen bonding to the metal centre. Ligand **68** has been previously reported although no NMR or trimerisation data was reported, ligands **69**, **146** and **147** are novel.[36]

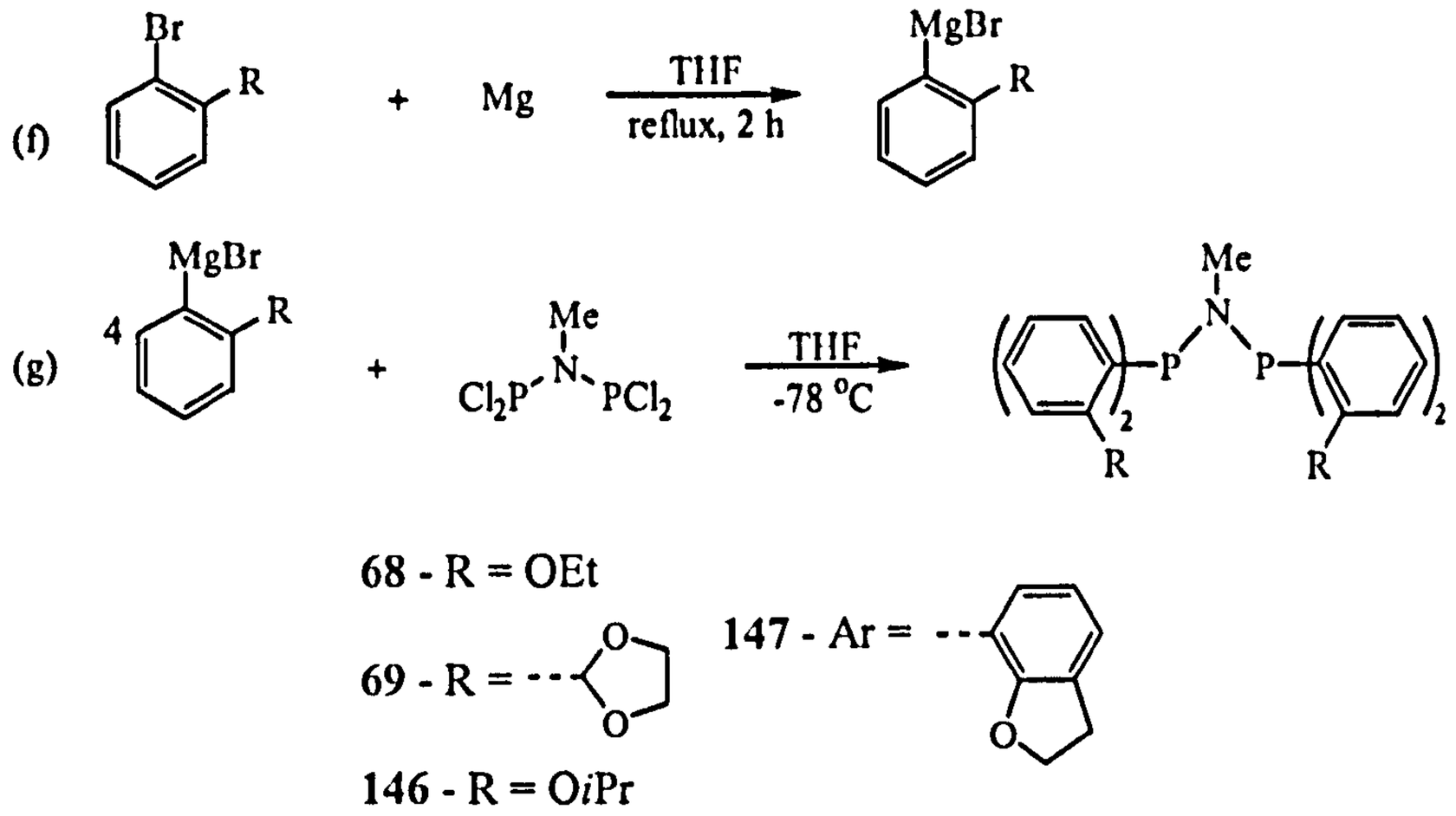
The PNP ligands were synthesised using general method 1, although the first stage is to synthesise the substituted bromobenzene starting materials as shown in Scheme 5.6. 2-Bromoethoxybenzene, **148**, and 2-bromoisopropoxybenzene, **149**, were synthesised using a method reported by Reitz and co-workers.[165] 7-Bromo-2,3-dihydrobenzofuran, **150**, was synthesised using a method reported by Thomas and coworkers.[166] 2-(2-Bromophenyl)-1,3-dioxolane, used to synthesise **151**, was commercially available.



Scheme 5.6 – Synthesis of Substituted Bromobenzene Starting Materials

In route (d) in Scheme 5.6 2-bromoethoxybenzene, **148**, and 2-bromoisopropoxybenzene, **149**, were synthesised by reacting bromophenol with bromoethane, in the presence of potassium carbonate in dimethylformamide (DMF). Route (e) in Scheme 5.6 shows the synthesis of 7-bromo-2,3-dihydrobenzofuran, **150**. This was achieved by reacting 2,6-dibromophenol with 1,2-dibromoethane in water to give 1,3-dibromo-2-(2-bromoethoxy)benzene, then adding *n*-butyllithium to cause cyclisation to occur and form 7-bromo-2,3-dihydrobenzofuran, **150**.

Substituted bromobenzene compounds **148, 149, 150** and **151** were used to synthesise PNP ligands **68, 146, 147** and **69** respectively as shown in Scheme 5.7.[161, 162]



Scheme 5.7 – Synthesis of PNP Ligands with Oxygen Donor Groups

The synthesis of PNP ligand **68** and **69** were successful and the ^{31}P NMR data of these two ligands is shown in Table 5.1, which also includes the ^{31}P NMR shift for *N,N*-bis(di-*ortho*-methoxyphenylphosphino)-methylamine, **1**.[37] ^{31}P NMR spectra of PNP ligands **68** and **69** show a singlet peak as both phosphorus atoms are equivalent.

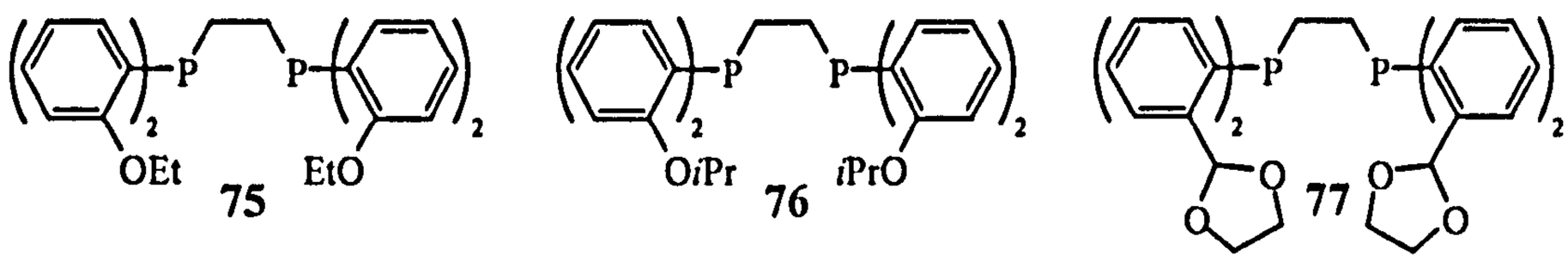
Table 5.1 – ^{31}P NMR Shifts for Novel PNP Ligands

Ligand	^{31}P Shift / ppm
1	52.3
68	56.3
69	53.9

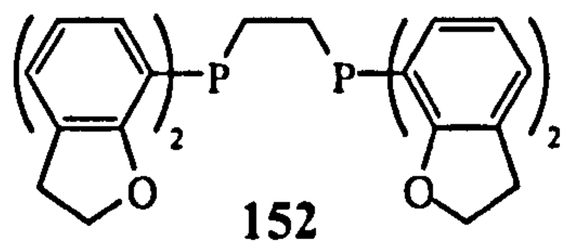
The ^{31}P NMR shifts of ligands **68** and **69** are 56.3 and 53.9 ppm respectively which is consistent with the shift shown for **1**. The synthesis of PNP ligands **146** and **147** was unsuccessful and it is unknown as to why this occurred. PNP synthesis has previously proved to be unpredictable depending on specific substitution patterns. It was thought that the ligands with bulky *ortho* substituents would be the difficult ligands to synthesise, but ligand **69** has the substituent with the highest steric bulk.

5.3.2. Synthesis Bis(diarylphosphino)ethane (dppe) Ligands

The target dppe based ligands to be synthesised are shown in Figure 5.5.



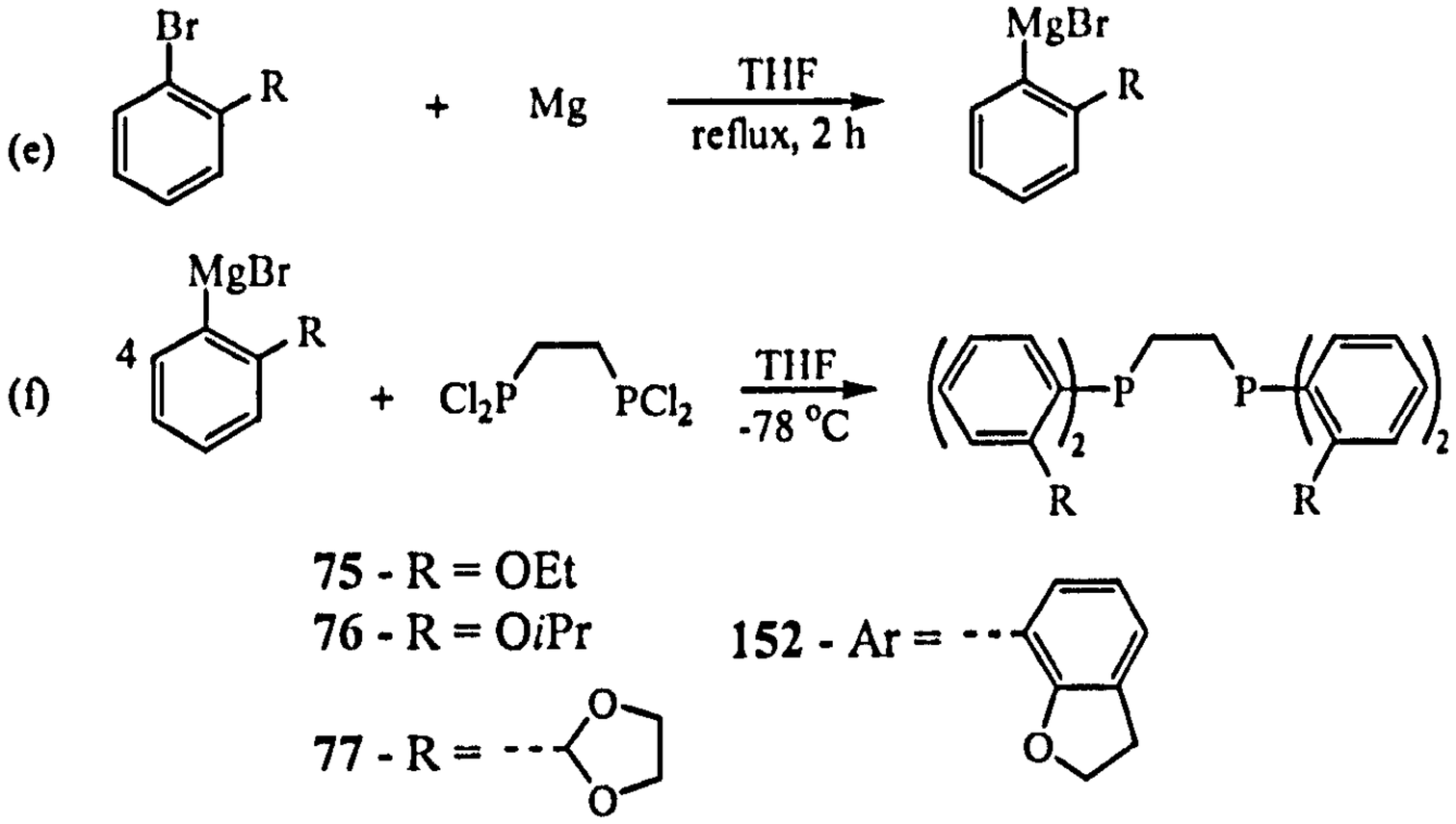
75 **76** **77**



152

Figure 5.5 – Dppe Ligands with Oxygen Donor Groups

Bis(di-*ortho*-ethoxyphenylphosphino)ethane, **75**, bis(di-*ortho*-isopropxyphenyl-phosphino)ethane, **76** and bis(di-*ortho*-(1,3-dioxolan-2-yl)phenylphosphino)ethane, **77** were synthesised using general method 1, as shown in Scheme 5.8, using a similar method as the synthesis of PNP ligands in Scheme 5.7. Bis(di-*ortho*-ethoxyphenylphosphino)ethane, **75** has been previously reported but ligands **76**, **77** and **152** are novel.[173] The *ortho* substituted bromobenzene derivatives, 2-bromoethoxybenzene (synthesis of ligand **75**), 2-bromoisopropoxybenzene (synthesis of ligand **76**) or 2-(2-bromophenyl)-1,3-dioxolane (synthesis of ligand **77**) starting materials were reacted with magnesium to form the corresponding Grignard reagent. Four equivalents of the Grignard reagent were then reacted with bis(dichlorophosphino)ethane in tetrahydrofuran to give the dppe ligand. The synthesis of ligand **152** was unsuccessful and as with the unsuccessful PNP ligands, it is unknown to why this synthesis was unsuccessful.



Scheme 5.8 – Synthesis of Dppe Ligands with Oxygen Donor Groups

As with PNP ligands, the ^{31}P NMR of dppe ligands **75** to **77** show a singlet due to equivalent phosphorus atoms, the values are shown in Table 5.2. The table includes the ^{31}P NMR shift for bis(di-*ortho*-methoxyphenylphosphino)ethane, **6**.[173]

Table 5.2 – ^{31}P NMR Shifts for Dppe Ligand 75 – 77

Ligand	^{31}P Shift / ppm
6	-30.5
75	-23.1
76	-24.1
77	-38.0

The ^{31}P NMR shifts for ligands **75**, **76** and **77** are -23.1 ppm, -24.2 ppm and 38.0 ppm respectively, which is consistent with ligand **6**. Ligand **77** shows the most negative shift, suggesting the phosphorus atoms are less deshielded for this dppe ligand than the other dppe derivatives shown. This may be because the 1,3-dioxolane groups in the *ortho* position of the phenyl rings is more electron donating than the methoxy, ethoxy or isopropoxy groups.

The molecular structure of ligand **77** is shown in Figure 5.6. The hydrogen atoms are omitted for clarity.

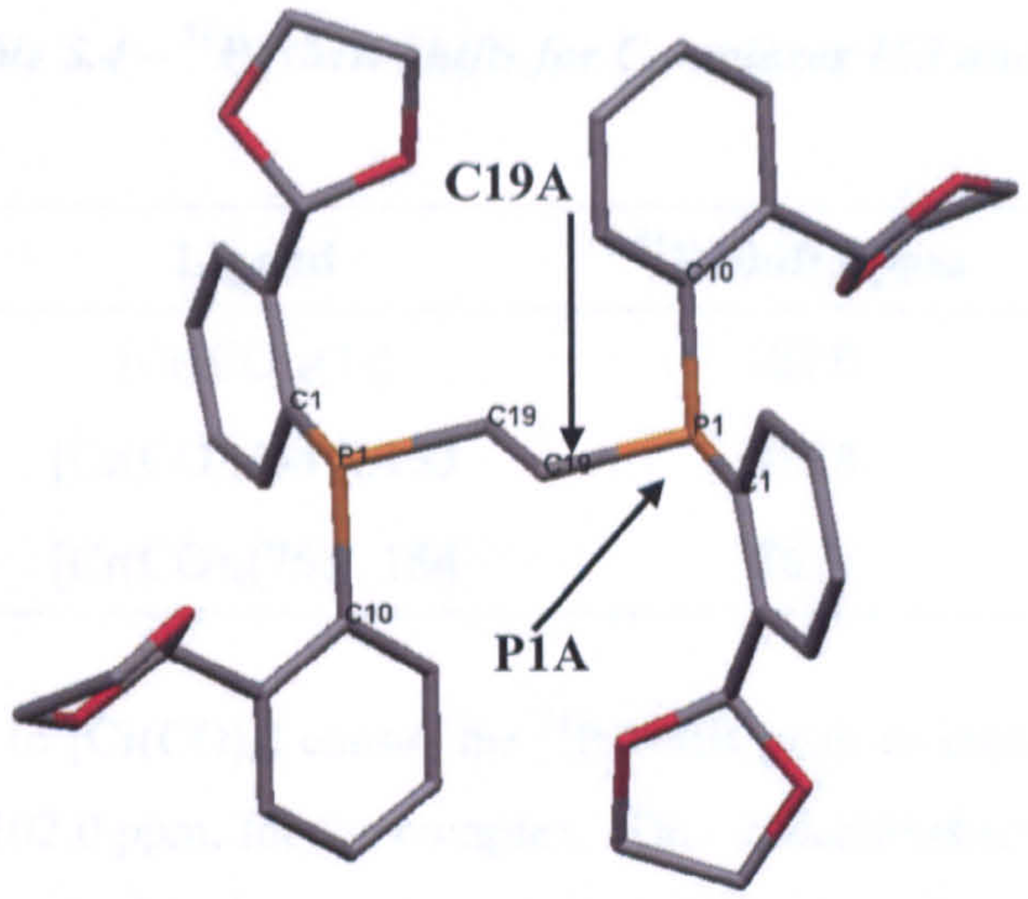


Figure 5.6 - Molecular Structure of Ligand 77

The molecular structure of ligand **77** shows the arrangement of 1,3-dioxolane groups around the ligand, with two phenyl groups in the plane of the carbon backbone and two phenyl ring in the plane of the P-C bond. A selection of bond lengths and angles are shown in Table 5.3.

Table 5.3 – Selected Bond Angles and Lengths of Bis(di-ortho-(1,3-dioxolan-2-yl)phenylphosphino)ethane 77

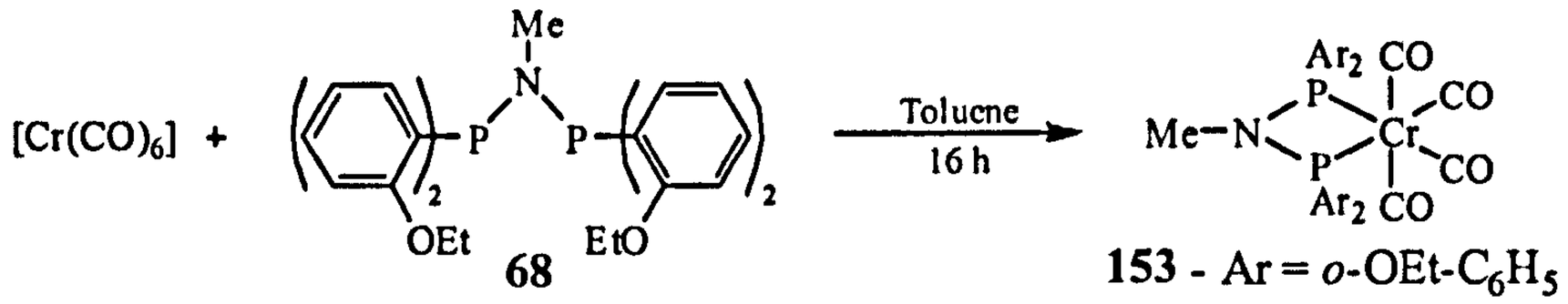
		Ligand 77
Bond Lengths / Å	P(1)-C(19)	1.849(15)
	P(1)-C(1)	1.846(15)
	P(1)-C(10)	1.849(15)
	C(19A)-C(19)	1.531(3)
Angles / °	P(1)-C(19)-C(19A)	110.15(12)
	C(10)-P(1)-C(1)	101.45(6)
	C(10)-P(1)-C(19)	101.46(7)
	C(1)-P(1)-C(19)	103.08(6)

The P(1)-C(19) bonds of 1.849(15) Å are consistent with a phosphorus-carbon single bond. The C(19A)-C(19) bond of 1.531(3) Å is consistent with a carbon-carbon single bond. The angle P(1)-C(19)-C(19A) of 110.15(12)° is in accordance with a tetrahedral arrangement of groups around the phosphorus atoms.

5.4. Chromium Carbonyl Phosphine Complexes

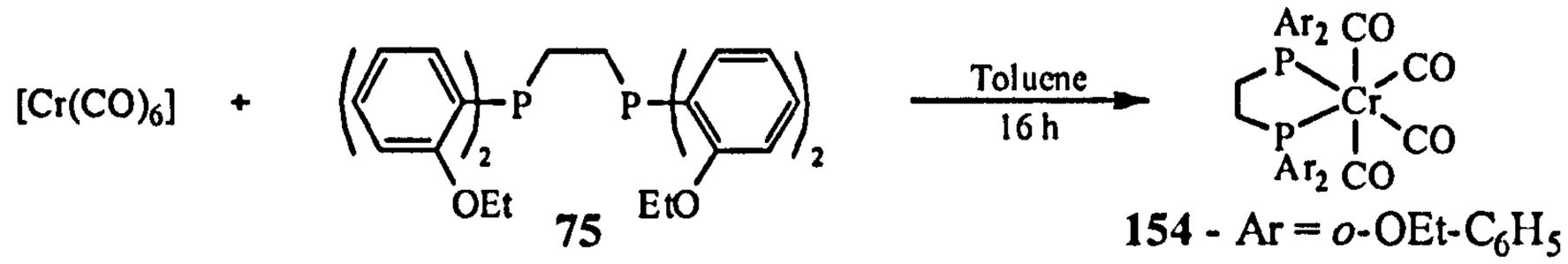
5.4.1. Synthesis

Chromium carbonyl complexes were synthesised using a method reported by Balakrishna and co-workers.[145] The chromium carbonyl complexes of **68** and **75** were synthesised as shown in Scheme 5.9 and Scheme 5.10.



Scheme 5.9 – Synthesis of [Cr(CO)$_4$(68)], 153

The synthesis of [Cr(CO)$_4$(**68**)], **153**, was achieved by refluxing [Cr(CO)$_6$] with the ligand in toluene overnight, giving a yellow solution. The compound was isolated by removal of the toluene under vacuum and the resulting solid was washed with dry methanol, giving a yellow solid. X-ray crystals were formed by slow diffusion of methanol into a concentrated dichloromethane solution of the complex.



Scheme 5.10 – Synthesis of [Cr(CO)$_4$(75)], 154

[Cr(CO)$_4$(**75**)] was synthesised using the same method as [Cr(CO)$_4$(**68**)], using [Cr(CO)$_6$] and ligand **75**, as shown in Scheme 5.10. The ^{31}P NMR spectra of complexes **153** and **154** showed one singlet peak, as the two phosphorus atoms are equivalent, the values are shown in Table 5.4, which also shows the ^{31}P shift for [Cr(CO)$_4$(**1**)] (see Table 4.1).

Table 5.4 – ^{31}P NMR Shifts for Complexes 153 and 154

Ligand	^{31}P Shift / ppm
$[Cr(CO)_4(\mathbf{1})]$	102.0
$[Cr(CO)_4(\mathbf{68})]$, **153**	103.8
$[Cr(CO)_4(\mathbf{75})]$, **154**	76.3

Bonding ligand **68** to $[Cr(CO)_6]$ causes the ^{31}P NMR peak to shift from 56.3 ppm, for the free ligand, to 102.0 ppm, for the complex. This is due to electron density from the phosphorus being donated to the metal centre and so the two phosphorus atoms become more deshielded. A similar shift is observed in comparing the ^{31}P NMR spectrum of ligand **75** to complex **154**.

5.4.2. Molecular Structures of Chromium Phosphine Carbonyl Complexes

The molecular structure of $[Cr(CO)_4(\mathbf{68})]$, **153** is shown in Figure 5.7. The hydrogen atoms and a dichloromethane molecule are omitted for clarity.

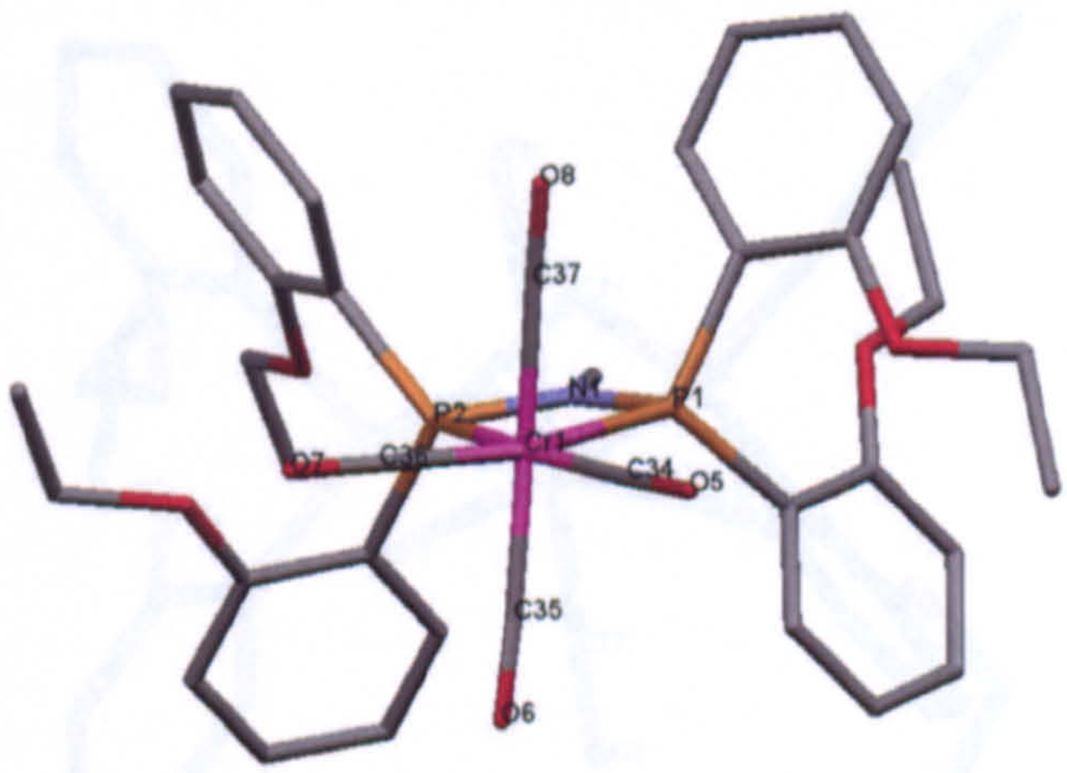


Figure 5.7 - Molecular Structure of $[Cr(CO)_4(68)]$, 153

Complex **153** adopts an octahedral arrangement of ligands around the chromium centre and crystallises with one molecule of dichloromethane in the asymmetric unit. The fold angle, which is the difference between the CrP_2 (P(1)-Cr(1)-P(2)) plane and the P_2N

(P(1)-N(1)-P(2)) plane, is 0.91° and comparing this to [Cr(CO)$_4$(**1**)], **133** with a fold angle of 2.6°, complex **153** has a very flat P(1)-Cr-P(2)-N(1) ring. As with complex **133,** the nitrogen is in sp^2 hybridisation, with the sum of the angles around the nitrogen atom being 359.9°. The bond angles and lengths are given in Table 5.5.

The molecular structures of [Cr(CO)$_4$(**75**)], **154** is shown in Figure 5.8. The hydrogen atoms are omitted for clarity. A selection of bond lengths and angles are shown in Table 5.5.

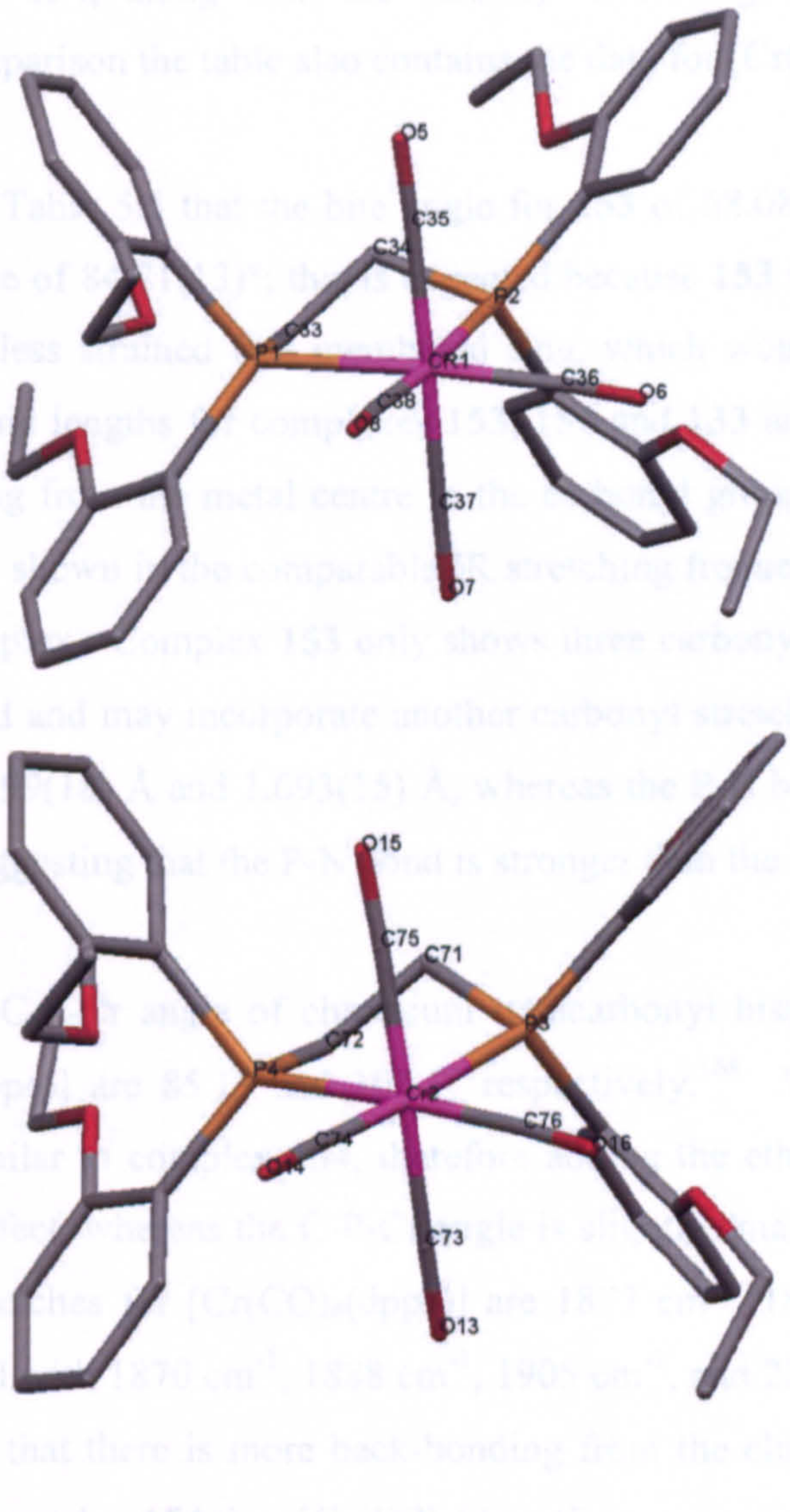


Figure 5.8 – Molecular Structure of [Cr(CO)$_4$(75)], 154

Complex **154** crystallises with two molecules in the asymmetric unit. The aryl rings adopt a similar conformation in each molecule, the difference appears in the orientation

of carbon backbone in the ligand. The fold angle between the P(1)-Cr(1)-P(2) plane and the P(1)-C(34)-P(2) plane in structure 1 is 17.63° and between the P(1)-Cr(1)-P(2) plane and the P(1)-C(35)-P(2) is 5.71°. Whereas the fold angles for P(3)-Cr(2)-P(2) and P(3)-C(71)-P(4) or P(3)-C(72)-P(4) in structure 2 are 12.22° and 18.26° respectively. Unlike the nitrogen in the backbone of the ligand in complex **153**, the two carbons in the backbone of the ligand in complex **154** have a sp^3 hybridisation.

Table 5.5 shows a selection of bond lengths and angles for chromium carbonyl complexes **153** and **154**, along with the carbonyl stretching frequencies for both complexes. For comparison the table also contains the data for $[Cr(CO)_4(1)]$.

It can be seen from Table 5.5 that the bite angle for **153** of 68.08(19)° is smaller than **154**, with a bite angle of 84.71(13)°; this is expected because **153** has a four-membered ring and **154** has a less strained five membered ring, which would give a larger bite angle. The C≡O bond lengths for complexes **153**, **154** and **133** are similar, suggesting that the back-bonding from the metal centre to the carbonyl groups is similar for each complex; this is also shown in the comparable IR stretching frequencies of the carbonyl groups for each complex. Complex **153** only shows three carbonyl peaks, but the peak at 1885 cm^{-1} is broad and may incorporate another carbonyl stretch. The P-N bonds in complex **153** are 1.699(18) Å and 1.693(15) Å, whereas the P-C bonds in complex **154** are about 1.84 Å, suggesting that the P-N bond is stronger than the P-C bond.

The bite angle and C-P-Cr angle of chromium tetracarbonyl bis(diphenylphosphino)-ethane, $[Cr(CO)_4(dppe)]$ are 85.1° and 107.5° respectively.[168] Within error the bite angle of dppe is similar to complex **154**, therefore adding the ethoxy groups does not have a significant effect, whereas the C-P-Cr angle is slightly smaller for complex **154**. The IR carbonyl stretches for $[Cr(CO)_4(dppe)]$ are 1877 cm^{-1}, 1899 cm^{-1}, 1914 cm^{-1}, 2009 cm^{-1}, compared with 1870 cm^{-1}, 1888 cm^{-1}, 1905 cm^{-1}, and 2002 cm^{-1} for complex **154**.[169] This shows that there is more back-bonding from the chromium centre to the carbonyl ligands in complex **154** than $[Cr(CO)_4(dppe)]$.

Table 5.5 – Selected Bond Angles, Bond Lengths and IR Stretches of Complexes 153 and 154, Along with Complex 133

	[Cr(CO)$_4$(68)] 153		[Cr(CO)$_4$(75)] 154		[Cr(CO)$_4$(1)] 133	
Bond Lengths / Å			Cr(1)-C(35)	1,882(15)		
			Cr(1)-C(36)	1.849(13)		
	Cr(1)-C(34)	1.857(2)	Cr(1)-C(37)	1.889(14)	Cr(1)-C(2)	1,878(3)
	Cr(1)-C(35)	1.896(2)	Cr(1)-C(38)	1.851(14)	Cr(1)-C(3)	1.891(3)
	Cr(1)-C(36)	1.857(2)	Cr(2)-C(73)	1.891(14)	Cr(1)-C(4)	1.862(3)
	Cr(1)-C(37)	1.886(2)	Cr(2)-C(74)	1.848(14)	Cr(1)-C(5)	1.858(3)
			Cr(2)-C(75)	1.880(13)		
			Cr(2)-C(76)	1.854(15)		
			C(35)-O(5)	1.146(17)		
			C(36)-O(6)	1.161(16)		
	C(34)-O(5)	1.157(3)	C(37)-O(7)	1.146(17)	C(2)-O(1)	1.156(4)
	C(35)-O(6)	1.150(3)	C(38)-O(8)	1.158(16)	C(3)-O(2)	1.154(4)
	C(36)-O(7)	1.158(3)	C(74)-O(14)	1.149(16)	C(4)-O(3)	1.146(4)
	C(37)-O(8)	1.150(3)	C(75)-O(15)	1.158(16)	C(5)-O(4)	1.155(4)
			C(76)-O(16)	1.160(16)		
			C(77)-O(17)	1.156(17)		
			Cr(1)-P(1)	2.391(4)		
	Cr(1)-P(1)	2.374(6)	Cr(1)-P(2)	2.402(4)	Cr(1)-P(2)	2.356(12)
	Cr(1)-P(2)	2.370(6)	Cr(2)-P(3)	2.385(4)	Cr(1)-P(2)	2.368(10)
			Cr(2)-P(4)	2.389(4)		

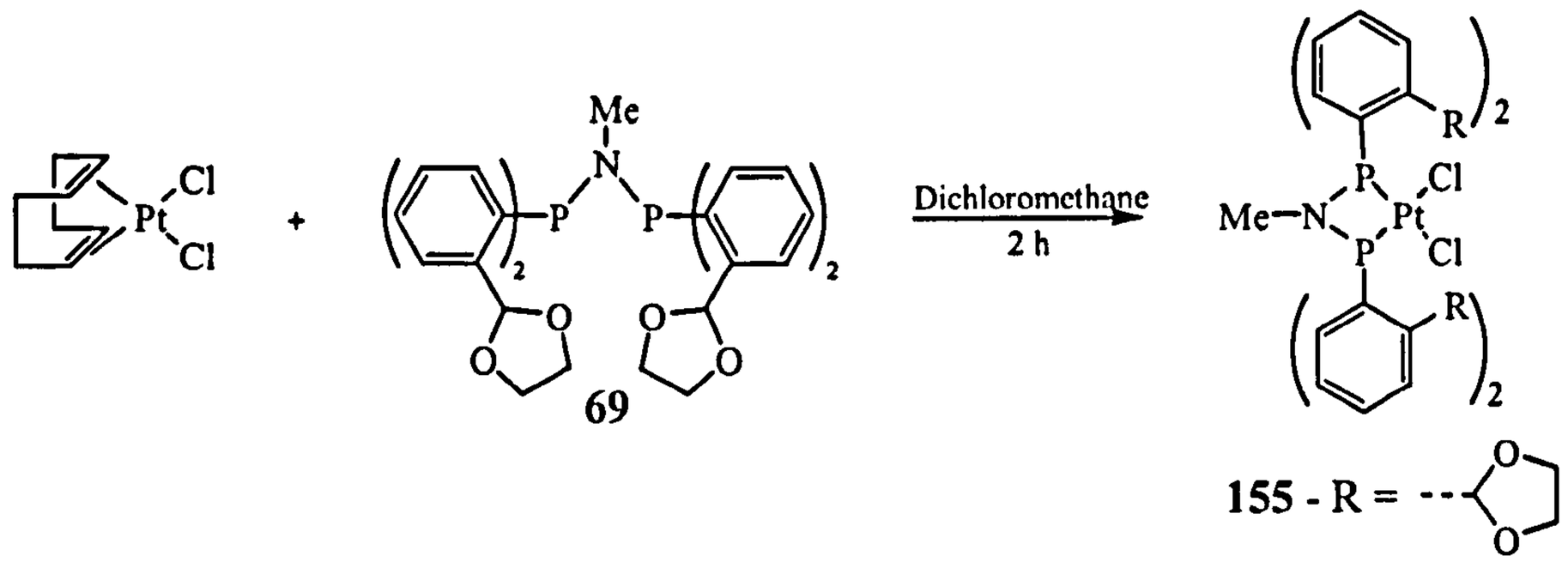
	[Cr(CO)$_4$(13)] 153		[Cr(CO)$_4$(27)] 154		[Cr(CO)$_4$(1)] 155	
Bond Length cont.	P(1)-N(1) P(2)-N(1)	1.699(18) 1.693(15)	P(1)-C(33) P(2)-C(34) P(3)-C(71) P(4)-C(72)	1.841(13) 1.841(13) 1.838(13) 1.843(13)	P(1)-N(1) P(2)-N(1)	1.700(15) 1.704(15)
	-		C(33)-C(34) C(71)-C(72)	1.534(18) 1.530(19)	-	
Angles / °	P(1)-Cr-P(2)	68.08(19)	P(1)-Cr(1)-P(2) P(3)-Cr(2)-P(4)	84.71(13) 85.36(13)	P(1)-Cr-P(2)	68.45(3)
	P(1)-N(1)-P(2)	103.02(10)	P(1)-C(33)-C(34) P(2)-C(34)-C(33) P(3)-C(71)-C(72) P(4)-C(72)-C(71)	109.10(9) 108.67(9) 108.91(8) 109.06(9)	P(1)-N(1)-P(2)	102.04(13)
C≡O IR Stretches / cm^{-1}	1885 (br), 1908, 2002		1870, 1888, 1905, 2002		1869, 1888, 1907, 2003	

5.5. Platinum Chloride Phosphine Complexes

This section investigates a series of platinum chloride PNP complexes. These complexes were synthesised to look at the structure of the ligand. Also the synthesis of the chromium carbonyl complexes of these ligands was unsuccessful as the ligands are too bulky.

5.5.1. Synthesis

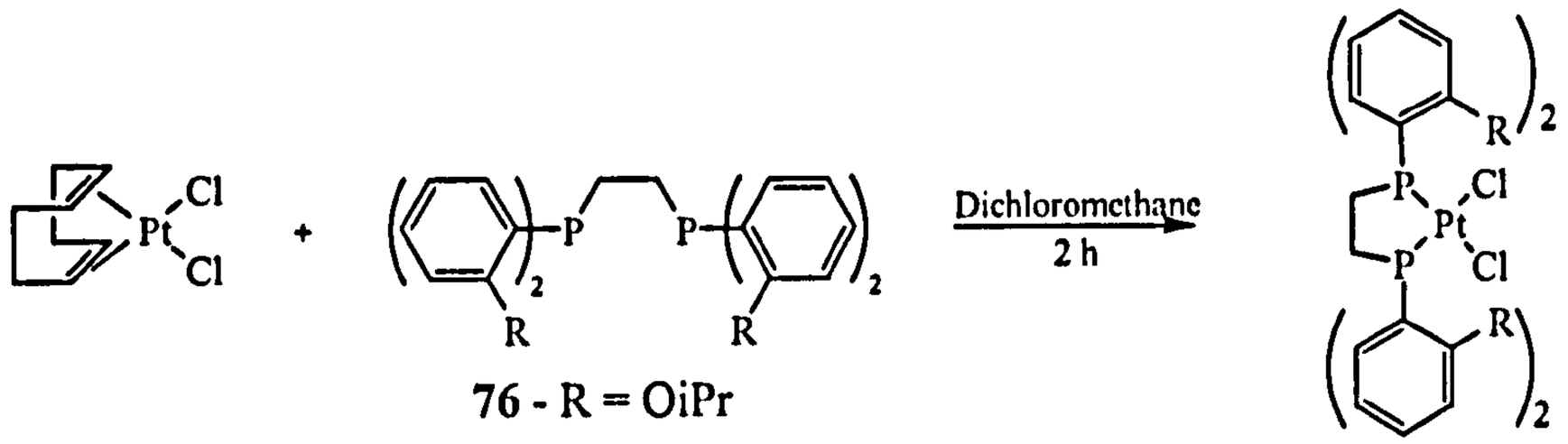
Ligand **69**, was reacted with $[PtCl_2(COD)]$ in dichloromethane under nitrogen, where COD is 1,5-cyclooctadiene, to give $[PtCl_2(69)]$. The reaction scheme is shown in Scheme 5.11.



Scheme 5.11 – Synthesis of $[PtCl_2(69)]$, 155

A white solid was obtained on removal of dichloromethane, which would only re-dissolve into dimethylsulfoxide (DMSO). The growth of crystals was attempted *via* a slow diffusion method, using a range of solvent systems and was unsuccessful.

The same method was used to synthesise $[PtCl_2(76)]$, **156**, and $[PtCl_2(77)]$, **157**, as shown in Scheme 5.12.



76 - R = OiPr

77 - R = ····O O

156 - R = OiPr

157 - R = ····O O

Scheme 5.12 – Synthesis of [$PtCl_2$(76)], 156 and [$PtCl_2$(77)], 157

The ^{31}P NMR of complexes **155**, **156** and **157** gave a singlet peak, due to equivalent phosphorus atoms, with platinum satellites. The ^{31}P NMR data in deuterated chloroform at 25 °C, is given in Table 5.6, along with the literature values for [$PtCl_2$(dppe)].[170]

Table 5.6 – ^{31}P NMR Shifts for Novel Platinum PNP or Dppe Complexes

Ligand	^{31}P Shift / ppm ($CDCl_3$)	Coupling Constant (J_{PPt}) / Hz
[$PtCl_2$(69)], **155**	16.2	3340
[$PtCl_2$(76)], **156**	47.6	3659
[$PtCl_2$(77)], **157**	44.6	3646
[$PtCl_2$(dppe)]	40.9	3618

The ^{31}P NMR shifts for complexes **156** and **157** are consistent with the literature values for [$PtCl_2$(dppe)]. The ^{31}P NMR shift for complex **155**, has a lower shift that the dppe analogue, **157**, suggesting that the phosphorus atoms in complex **157** is more deshielded than complex **155**. The P-Pt coupling constants for the three complexes are typical of the coupling constants for Pt-phosphine complexes with a *cis* arrangement; which is expected due to the bidentate phosphine ligands.[170]

5.5.2. Molecular Structure of [$PtCl_2$(76)]

X-ray quality crystals of [$PtCl_2$(**76**)], **156**, were grown from a slow diffusion of acetone into a concentrated DMSO solution of the complex, giving white crystals, the molecular structure is shown in Figure 5.9. Hydrogen atoms have been removed for clarity.

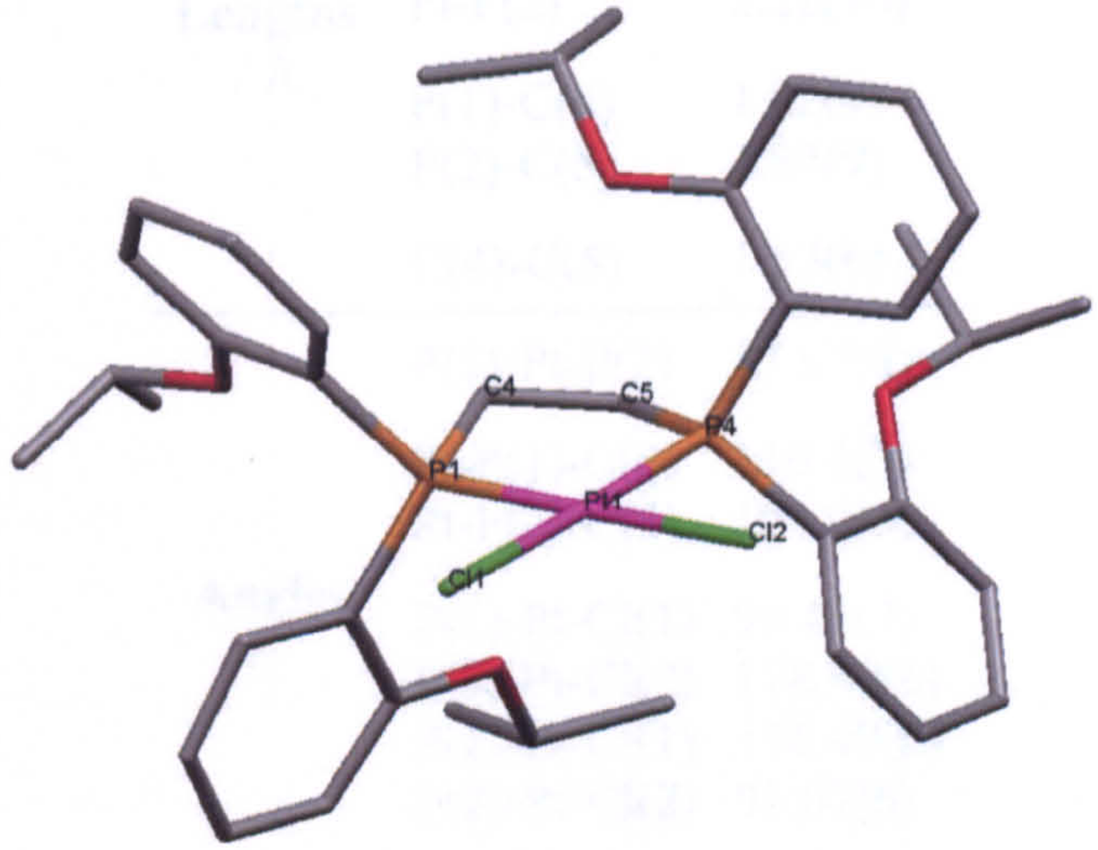


Figure 5.9 – Molecular Structure of [$PtCl_2$(76)], 156

The molecular structure of [$PtCl_2$(**76**)], **156**, shows a square planar arrangement of ligands around the metal centre, with the aryl groups of the ligand above and below the plane of the molecule. In Figure 5.9 P(4) has been mislabelled and should be P(2), P(2) will be used when referring to this atom.

As expected, the carbon backbone of the phosphine ligand is bent with C(4) above the plane of the metal-chlorine bonds and C(5) below the plane. The fold angle between the P(1)-Pt(1)-P(2) plane and the P(1)-C(4)-P(2) plane is 6.48° and between the P(1)-Pt(1)-P(2) plane and the P(1)-C(5)-P(2) is 5.54°. A selection of bond length and angles is shown in Table 5.6.

Table 5.7 – Selected Bond Angles and Lengths of [$PtCl_2$(76)], 156

		[$PtCl_2$(76)] 156
Bond Lengths / Å	Pt-Cl(1)	2.38(16)
	Pt-Cl(2)	2.37(15)
	Pt-P(1)	2.23(16)
	Pt-P(2)	2.22(16)
	P(1)-C(4)	1.82(9)
	P(2)-C(5)	1.84(9)
	C(4)-C(5)	1.53(6)
Angles / °	P(1)-Pt-P(2)	87.97(4)
	Pt-P(1)-C(4)	110.1(3)
	Pt-P(2)-C(5)	109.9(3)
	P(1)-Pt-Cl(1)	90.43(7)
	P(1)-Pt-Cl(2)	178.99(6)
	P(2)-Pt-Cl(1)	178.40(6)
	P(2)-Pt-Cl(2)	91.07(6)
	Cl(1)-Pt-Cl(2)	90.53(4)

The bite angle, P(1)-Pt-P(2) is 87.97(4)°, which is similar to the P(1)-Cr-P(2) angle in [$Cr(CO)_4$(**75**)], **134**. The P(1)-C(4), P(2)-C(5) and C(4)-C(5) bond lengths are also similar to the corresponding bond lengths in complex **134**.

5.6. Ethene Trimerisation With PNP and Dppe Ligands

PNP ligands **68** and **69** and dppe derivatives **75** to **77** were tested for ethene trimerisation using the system shown in Scheme 1.8.[2] For runs 5.1 to 5.6, 0.02 mmol of [$CrCl_3(thf)_3$], 0.02 mmol of ligand and 300 eq of methylaluminoxane (MAO) were used, under 1 bar of ethene at room temperature. The productivity was calculated from the mass gain of the reaction vessel for runs 5.1 to 5.6. The 1-hexene (1-C_6) selectivity is given within the C_6 fraction.

Table 5.8 – Ethene Trimerisation with PNP and Dppe Ligands 68, 69 and 75 – 77 at Low Ethene Pressure

Run	Ligand	Productivity[a] / g (g Cr h)$^{-1}$	Product Distribution / wt %			
			C_6	1-C_6[c]	C_{10}	C_{14+}
5.1	68	7404	63.2	91.2	33.3	3.5
5.2	69	0	-	-	-	-
5.3	75	0	-	-	-	-
5.4	76	0	-	-	-	-
5.5	77	0	-	-	-	-
5.6	1	8654	73.0	86.1	25.0	2.0

[a] within C_6 fraction

Table 5.8 shows the results for ethene trimerisation using ligands **68, 69** and **75** to **77**. Run 5.6 gives the results for **1** as a comparison. Ligand **68** was found to be active for ethene trimerisation, with a productivity of 7404 g (g Cr h)$^{-1}$ obtained. The system showed a selectivity of 63.2 % towards C_6 fraction, of which 91.2 % was 1-hexene. Ligand **68** gives a lower productivity than **1**, although the selectivity towards 1-C_6 within C_6 fraction was 91.2 % for **68**, whereas for **1** the selectivity is 86.1 % under the same conditions. Unlike other PNP ligands previously tested (apart from **1**), a high productivity towards ethene was given at room temperature and under 1 bar of ethene. Other PNP ligands tested by Bollmann and co-workers[41, 42, 47] and Wass and co-workers needed a high ethene pressure for hexene to be produced.[1, 4,] Ligand **69** was shown to be inactive for ethene trimerisation under 1 bar of ethene. Ligands **75** to **77** were also inactive for ethene trimerisation, this is consistent with the data reported by Wass and co-workers, where ligand **5** (bis(di-*ortho*-methoxyphenylphosphino)ethane) was inactive under 1 bar of ethene.

The same set of ligands was tested for trimerisation at a high ethene pressure. The results are shown in Table 5.9. The reaction conditions for the high pressure runs is 0.01 mmol of [$Cr(acac)_3$], 0.01 mmol of ligand and 300 equivalents of MAO, under 45 bar of ethene at 45 °C. Mesitylene was used as the internal standard and for comparison, run 5.12 shows the results obtained for the system using ligand **1**.

Table 5.9 – Ethene Trimerisation with PNP and Dppe Ligands 68, 69 and 75 – 77 at High Ethene Pressure

Run	Ligand	Productivity / g (g Cr h)$^{-1}$	Product Distribution / wt %			
			C_6	1-C_6^c	C_8	C_{10+}
5.7	68	1282	87.6	79.1	0	12.4
5.8	69	0	50.7	62.1	36.7	12.6
5.9	75	0	-	-	-	-
5.10	76	0	-	-	-	-
5.11	77	0	-	-	-	-
5.12	1	720	98.9	73.2	1.1	0

[a] within C_6 fraction

The system using PNP ligand **68**, with OEt groups gave a high productivity than ligand **1**, of 1282 g (g Cr h)$^{-1}$. A selectivity to hexene of 87.6 % was observed, of which 79.1 % is 1-hexene, this system has a lower hexene selectivity than the ligand **1** system. Ligand **69** showed an activity for ethene trimerisation, with a selectivity to hexene of 50.7 %, although a statistical distribution of products was observed including 36.7 % C_8 and 12.6 % C_{10+} materials. As with the reactions at low ethene pressure, ligands **75** to **77** were found to be inactive for ethene trimerisation. These ligands were also tested for isoprene trimerisation and ethene/styrene cotrimerisation and are shown in Chapter 2 and 3.

5.7. Summary

One of the best systems for the trimerisation of ethene uses [$CrCl_3(thf)_3$], **1** and MAO.[1, 4] The PNP ligand in this system contains methoxy groups on the *ortho* position of the phenyl groups, in the molecular structure one of [$CrCl_3$(1)], one methoxy (OMe) group acts as a pendant ligand to the chromium centre, forming an octahedral arrangement, which can stabilise intermediates during catalysis.[5] A selection of methods for synthesising PNP ligands have been reported by reported by Dossett and co-workers,[33] Cooley and co-workers,[34] Bollmann and co-workers,[41, 42, 47] and Balakrishna and co-workers.[1345]

A range of PNP ligands and dppe derivatives, with *ortho* oxygen donor groups on the aryl rings, were synthesised and the method used involved the reaction of four equivalents of a Grignard reagent with bis(dichlorophosphino)methylamine. The ligands synthesised were **68** and **69** and **75** to **77** and the molecular structure of **77** was given with 1,3-dioxolane groups attached to the *ortho* position of the aryl rings. Ligands **68** and **75** were coordinated to $[Cr(CO)_6]$, giving yellow solids $[Cr(CO)_4(\mathbf{68})]$, **153** and $[Cr(CO)_4(\mathbf{75})]$, **154**. The molecular structures of both complexes showed an octahedral arrangement around the chromium centre. The carbonyl bond lengths and IR stretching frequencies of both complexes are similar, although the bite angle of **154** is larger than **153**. Ligands **69**, **76** and **77** were reacted with $[PtCl_2(COD)]$ giving $[PtCl_2(\mathbf{69})]$, **155**, $[PtCl_2(\mathbf{76})]$, **156** and $[PtCl_2(\mathbf{77})]$, **157**. The molecular structure of **156** showed a square planar arrangement around the platinum centre.

Ligands **68**, **69** and **75** to **77** were tested for activity towards ethene trimerisation. It was found that **68** was active, giving a productivity of 7404 g (g Cr h)$^{-1}$. The system using **68** gave a lower productivity than **1**, suggesting that although the OEt group may act as a pendant group to the chromium centre, the OMe group is a better pendant ligand. The phosphine ligands tested were found to be inactive towards ethene trimerisation. At high ethene pressure the system using ligand **68** gave a higher productivity than ligand **1** and ligands **69** and **75** to **77** were found to be inactive. The ligands synthesised in this chapter were also tested for ethene/styrene cotrimerisation and isoprene trimerisation.

Chapter 6

Experimental

6.1. General Experimental Information

All procedures were carried out under an inert atmosphere using standard Schlenk line and cannula techniques. Chemicals were obtained from Sigma Aldrich, Alfa Aesar, Strem and Fisher Scientific and unless otherwise stated were used without further purification. All solvents were purified using an Anhydrous Engineering Grubbs-type solvent system. The molecular weight of methylaluminoxane (MAO) was taken to be 58 g mol^{-1}, corresponding to a (CH_3-Al-O) unit. Cotrimerisation and trimerisation products were analysed by GC-MS and GC-FID (Hewlett Packard Series), mesitylene was used as an internal standard and alkane standards were obtained from Sigma Aldrich. The temperature program used was: starting at 40 °C and rising to 80 °C at 2 °C min^{-1} and then to 300 °C at 10 °C min^{-1}. Infra-red spectra were recorded on a Perkin-Elmer 1600 series FTIR Spectrometer in dichloromethane. NMR spectra were recorded on a JEOL ECP 300 spectrometer at 300 MHz (^{1}H) and 121 MHz (^{31}P) and a JEOL delta 400 spectrometer at 400 MHz (^{1}H) and 100.5 MHz (^{13}C {1H}), in deuterated solvent. ^{1}H and ^{13}C {^{1}H} NMR spectra are referenced relative to high frequency of residual solvent and ^{31}P NMR spectra are referenced relative to high frequency of 85 % H_3PO_4. Electrochemical studies were carried out using an EG&G model 273A potentiostat linked to a computer using EG&G Model 270 Research Electrochemistry software in conjunction with a three-electrode cell. The working electrode was a platinum disc (1.6 mm diameter) and the auxiliary electrode a platinum wire. The reference was an aqueous saturated calomel electrode (SCE) separated from the test solution by a fine frit and an agar bridge saturated with KCl. Solutions were 1.0 x 10^{-3} mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in [NBu$^n_4$][PF_6] as the supporting electrolyte, the solvent used was CH_2Cl_2. Under these conditions, $E^{0'}$ for the one electron oxidation of [Fe(η^5-C_5Me_5)$_2$] added to the test solutions as internal calibrants is -0.08 V.[171] Unless specified all $(E_p)_{red}$, $(E_p)_{ox}$ and $E^{0'}$ values are at a scan rate, ν of 200 mV s^{-1}. Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemistry at the University of Bristol. Crystal structures were determined by Mairi Haddow and Stephen Mansell. High pressure reactions were performed in parallel using a Baskerville 10 multicell autoclave.

6.2. Ligand Synthesis

This section gives the experimental data for the ligands used in Chapter 2 and 3.

6.2.1. General Methods of Ligand Synthesis

6.2.1.1. General Method 1 – Synthesis of *N,N*-bis(di-*ortho*-methoxyphenylphosphino)methylamine, 1

(a) *N,N*-bis(dichlorophosphino)methylamine

The synthesis of $Cl_2PN(R)PCl_2$ compounds was reported by Nixon, where R is an alkyl group.[161, 162]

Methylamine hydrochloride (10 g, 0.15 mol) was dried under vacuum overnight to remove any excess water. To this was added degassed 1,1,2,2-tetrachloroethane (120 mL) under nitrogen. Phosphorus trichloride (53 mL, 0.60 mol) was added and the mixture was stirred under reflux for 11 d. The reaction was allowed to cool and excess phosphorus trichloride and solvent were removed under vacuum into the main trap, giving a brown oil. A second nitrogen trap was added and the product was distilled under a static vacuum at 120 °C. Remaining solvent was removed by heating the liquid under nitrogen to 70 °C giving a colourless liquid (5.25 g, 28 mmol, 19 %).

Analytical data matched reported literature values:[161]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.22 (s, 3H, C*H*$_3$)

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 160.8 (s).

(b) Preparation of (*ortho*-methoxy)phenylmagnesium bromide

A solution of 2-bromoanisole (6 mL, 48 mmol) in tetrahydrofuran (10 mL) was added drop-wise to magnesium turnings (2.5 g, 0.10 mol) in tetrahydrofuran (20 mL), a vigorous reaction ensued. Once addition was complete, the mixture was heated under reflux for 2 h and then filtered via a cannula to give a brown solution.

(c) Preparation *N,N*-bis(di-*ortho*-methoxyphenylphosphino)methylamine, **1**

The synthesis of *N,N*-bis(di-*ortho*-methoxyphenylphosphino)methylamine, **1**, was adapted from a method reported by Cooley and co-workers.[34] The Grignard reagent, *ortho*-methoxyphenylmagnesium bromide (80 mmol) in tetrahydrofuran (30 mL) was added drop-wise, to *N,N*-bis(dichlorophosphino)methylamine (2.7 g, 0.012 mol) in tetrahydrofuran (20 mL) at -78 °C under nitrogen. The solution was stirred for 2 h and then allowed to warm to room temperature. Solvent was removed under vacuum and the resulting brown solid was repeatedly washed with cold methanol, to give a white solid (2.21 g, 4.3 mmol, 35 %).

Analytical data matched reported literature values:[37, 42]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.42 (s, 3H, NCH_3), 3.59 (s, 12H, OCH_3), 6.83 – 6.88 (m, 8H, Ar*H*), 7.06 – 7.10 (m, 4H, Ar*H*), 7.24 – 7.32 (m, 4H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 52.3 (s).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 33.8 (t, $^{2}J_{CP}$ = 5.4 Hz, NCH_3), 55.1 (s, OCH_3), 109.8 (s, *C*H), 120.0 (s, *C*H), 126.9 (t, J_{CP} = 4.6 Hz, *C*H), 129.8 (t, *C*H), 132.9 (s, *C*O), 160.6 (t, J_{CP} = 8.5 Hz, *C*P).

Elemental Analysis: $C_{29}H_{31}NO_4P_2$ calcd (%) C 67.04, H 6.02, N 2.69, found (%) C 67.48, H 5.55, N 2.59.

MS (+ESI): 520 $[M]^+$.

6.2.1.2. General Method 2 - *N,N*-bis(diphenylphosphino)isopropylamine, 19

The synthesis of *N,N*-bis(diphenylphosphino)isopropylamine, **19**, was adapted from a method reported by Bollmann and co-workers[41, 42, 47] and Balakrishna and co-workers.[161] Isopropylamine (0.94 mL, 11 mmol) was added drop-wise to a solution of diphenylphosphine chloride (4.1 mL, 22.7 mmol) and triethylamine (15 mL, 0.1 mol) in dichloromethane (80 mL) at -30 °C. Once addition was complete the solution was

stirred for 30 min then the ice bath was removed. The solution was stirred for a further 16 h at room temperature, after which the solution was filtered to remove triethylammonium chloride. Water (30 mL) was added and the aqueous layer was extracted with dichloromethane (2 x 10 mL). The organic layers were combined, dried over magnesium sulphate and filtered under nitrogen. The solvent was then removed under vacuum and the product was recrystalised from hot ethanol, giving a white crystalline solid (3.35 g, 7.84 mmol, 71 %).

Analytical data matched reported literature values:[42, 161]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.17 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, C*H*$_3$), 3.78 (sept, $^{2}J_{HH}$ = 6.6 Hz, 1H, NC*H*), 7.20 – 7.39 (m, 20H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 50.0 (br).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 24.5 (t, $^{3}J_{CP}$ = 6.2 Hz, *C*H$_3$), 52.0 (t, $^{2}J_{CP}$ = 10.0 Hz, NCH), 128.1 (d, J_{CP} = 6.2 Hz, *C*H), 126.6 (s, *C*H), 133.0 (d, J_{CP} = 22.3 Hz, *C*H), 140.0 (d, J_{CP} = 13.8 Hz, *C*P).

Elemental Analysis: $C_{27}H_{27}NP_2$ calcd (%) C 75.86, H 6.37, N 3.28, found (%) C 76.87, H 6.83, N 2.99.

MS (+ESI): 427 $[M]^+$.

6.2.1.3. General Method 3 – *N,N*-bis(di-*ortho*-ethylphenylphosphino)methylamine, 3

The synthesis of *N,N*-bis(di-*ortho*-ethylphenylphosphino)methylamine, **3**, was adapted from a method reported by Bollmann and co-workers[41, 42, 47] and Cooley and co-workers.[34]

(a) Preparation of 2-ethylphenylmagnesium bromide

A solution of 2-ethylbenzene (5.0 mL, 36.0 mmol) in tetrahydrofuran (10 mL) was added drop-wise to magnesium turnings (2.5 g, 0.10 mol) in tetrahydrofuran (20 mL), a vigorous reaction ensued. Once addition was complete, the mixture was heated under reflux for 2 h and then filtered via a cannula to give a brown solution.

(b) Synthesis of di(2-ethylphenyl)phosphine bromide

2-Ethylphenylmagnesium bromide (36.0 mmol) in tetrahydrofuran (30 mL) was added drop wise to a solution of phosphorus tribromide (4.9 mL, 18.0 mmol) in tetrahydrofuran (20 mL) at -78 °C under nitrogen. Once addition was complete the solution was allowed to warm to room temperature and stirred overnight. The solution was filtered and the solvent was removed to give an orange oil. The crude product was used in the next stage without further purification.

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 66.8 (s)

(c) Synthesis of *N,N*-bis(di-*ortho*-ethylphenylphosphino)methylamine, **3**

A solution of methylamine (2M in tetrahydrofuran, 1.5 mL, 3.0 mmol) and triethylamine (15 mL, 0.1 mol) in dichloromethane (10 mL), was slowly added to a solution of di(2-ethylphenyl)phosphine bromide in dichloromethane (2.16g, 10 mmol), at -78 °C under nitrogen. Once addition was complete the solution was allowed to warm to room temperature and was stirred overnight. The solution was filtered to remove magnesium chloride and the solvent was removed to give a yellow oil. The crude product was triturated with cold methanol and dried under *vacuo*, giving a white solid (0.66 g, 1.3 mmol, 43 %).

Analytical data matched reported literature values:[34, 41]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.13 (t, $^{3}J_{HH}$ = 7.5 Hz, 12H, CH_2CH_3), 1.45 (t, $^{3}J_{HH}$ = 7.3 Hz, 8H, CH_2CH_3), 3.12 – 3.16 (m, 3H, NCH_3) 7.02 – 7.10 (m, 8H, Ar*H*), 7.28 – 7.35 (m, 8H, Ar*H*).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 14.9 (s, CH_3), 27.4 (s, CH_2CH_3), 46.2 – 46.3 (m, NCH_3), 125.2 (s, *C*H), 128.5 (s, *C*H), 129.1 (s, *C*H), 132.2 (s, *C*H), 136.6 – 136.7 (m, *C*H), 147.2 (d, J_{CP} = 13.8 Hz, *C*P).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 56.8 (s) ppm.

Elemental Analysis: $C_{33}H_{39}NP_2.CH_2Cl_2$ calcd (%) C 68.44, H 6.93, N 2.34, found (%) C 66.70, H 7.39, N 2.03.

MS (+EI): 511 $[M]^+$, 482 $[M\text{-}CH_2CH_3]^+$, 406 $[M\text{-}Ar]^+$, 270 $[(Me)NPAr_2]^+$, (Ar = (*o*-$CH_2CH_3)C_6H_4$).

6.2.2. *N,N*-bis(diarylphosphino)alkylamine Ligands

6.2.2.1. *N,N*-bis(di-*para*-methoxyphenylphosphino)methylamine, 4

Synthesised by general method 1, using 4-bromoanisole (6.0 mL. 50 mmol), magnesium turnings (2.5 g, 0.10 mol), *N,N*-bis(dichlorophosphino)methylamine (1.8 g, 7.7 mmol) and tetrahydrofuran (40 mL), giving a white solid (1.7 g, 3.3 mmol, 43 %).

Analytical data matched reported literature values:[42]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.51 (s, 3H, NC*H*$_3$), 3.74 (s, 12H, OC*H*$_3$), 6.70 – 7.00 (m, 8H, Ar*H*), 7.18 – 7.25 (m, 4H, Ar*H*), 7.42 – 7.80 (m, 4H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 71.0 (s).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 31.0 – 31.2 (m, NCH_3), 55.2 (s, OCH_3), 109.8 (s, *C*H), 113.7 – 114.1 (m, *C*H), 134.9 (t, J_{CP} = 11.5 Hz, *C*O), 160.1 (t, J_{CP} = 8.5 Hz, *C*P).

Elemental Analysis: $C_{29}H_{31}NO_4P_2.CH_2Cl_2$ calcd (%) C 59.61, H 5.50, N 2.32, found (%) C 59.95, H 4.90, N 3.26.

MS (+EI): 519 $[M]^+$.

6.2.2.2. *N,N*-bis(di-*ortho*-methylphenylphosphino)methylamine, 10

Synthesised by general method 1, using 2-bromotoluene (3.6 mL, 30 mmol), magnesium turnings (3.6 g, 0.12 mol), *N,N*-bis(dichlorophosphino)methylamine (1.5 g, 6.0 mmol) and tetrahydrofuran (40 mL), giving a white solid (2.47 g, 5.4 mmol, 90 %).

Analytical data matched reported literature values:[34, 41]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.19 (s, 12H, CH_3), 2.57 (t, $^3J_{HP}$ = 3.0 Hz, 3H, NCH_3), 7.08 – 7.12 (m, 6H, Ar*H*), 7.20 – 7.30 (m, 10H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 57.6 (s).

^{13}C NMR ($CDCl_3$, 67 MHz): δ = 21.3 (t, $^2J_{CP}$ = 10.7 Hz, *C*H_3), 30.0 (s, NCH_3), 125.3 (s, *C*H), 128.8 (s, *C*H), 130.6 (t, J_{CP} = 2.3 Hz, *C*H), 131.5 – 131.6 (m, *C*H), 136.6 – 136.7 (m, *C*H), 141.3 (d, J_{CP} = 13.8 Hz, *C*P).

Elemental Analysis: $C_{29}H_{31}NP_2.CH_2Cl_2$ calcd (%) C 66.67, H 6.15, N 2.59, found (%) C 65.81, H 6.53, N 2.50.

MS (+EI): 455 $[M]^+$, 440 $[M\text{-}CH_3]^+$, 364 $[M\text{-}Ar]^+$.

6.2.2.3. *N,N*-bis(diphenylphosphino)methylamine, 17

Synthesised by general method 2, using methylamine (2M in tetrahydrofuran, 5.5 mL, 11 mmol), diphenylphosphine chloride (4.1 mL, 22.7 mmol) and triethylamine (15 mL, 0.1 mol) in dichloromethane (2 x 20 mL) giving a white solid (1.16 g, 2.9 mmol, 25 %).

Analytical data matched reported literature values:[42]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.32 (t, J_{HP} = 3.0 Hz, 3H, NC*H*$_3$), 7.25 – 7.35 (m, 20H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 73.5 (s).

^{13}C NMR ($CDCl_3$, 67 MHz): δ = 32.6 (t, $^{2}J_{CP}$ = 5.6 Hz, NCH_3), 128.2 (t, J_{CP} = 3.1 Hz, *C*H), 128.3 (s, *C*H), 132.4 (t, J_{CP} = 10.2 Hz, *C*H), 139.8 (d, J_{CP} = 7.2 Hz, *C*P).

Elemental Analysis: $C_{25}H_{23}NP_2$ calcd (%) C 75.18, H 5.80, N 3.51, found (%) C 74.59, H 4.97, N 3.96.

MS (+ESI): 400 $[M]^+$, 386 $[M\text{-}CH_3]^+$, 246 $[M\text{-}2Ph]^+$.

6.2.2.4. *N,N*-bis(diphenylphosphino)ethylamine, 63

Synthesised by general method 2, using ethylamine (2M in THF, 3.5 mL, 7 mmol), diphenylphosphine chloride (2.5 mL, 14.0 mmol) and triethylamine (10 mL, 66 mmol) in dichloromethane (2 x 20 mL) giving a white solid (1,92 g, 4.6 mmol, 66 %).

Analytical data matched reported literature values:[172]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.69 (t, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_2CH_3), 3.24 – 3.35 (m, 2H, NCH_2CH_3), 7.23 – 7.25 (m, 12H, Ar*H*), 7.33 – 7.37 (m, 8H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 62.4 (s).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 16.2 (t, $^{3}J_{CP}$ = 3.0 Hz, CH_3), 47.2 (t, $^{2}J_{CP}$ = 11.0 Hz, NCH_2), 127.9 – 128.0 (m, *C*H), 128.5 (d, J_{CP} = 11.6 Hz, *C*H), 132.6 (t, J_{CP} = 10.8 Hz, *C*H), 139.5 – 139.6 (m, *C*P).

Elemental Analysis: $C_{27}H_{27}NP_2.½CH_3OH$ calcd (%) C 74.10, H 6.33, N 3.26, found (%) C 74.15, H 6.49, N 4.19.

MS (+EI): 413 $[M]^+$, 384 $[M\text{-}CH_2CH_3]^+$.

6.2.2.5. *N,N*-bis(diphenylphosphino)-(*S*)-(+)-α-methylbenzylamine, 64

Synthesised by general method 2, using (*S*)-(+)-α-methylbenzylamine (2.5 mL, 20 mmol), diphenylphosphine chloride (2.7 mL, 15 mmol) and triethylamine (15 mL, 0.1 mol) in dichloromethane (2 x 20 mL) giving a white solid (4.6 g, mmol, 47 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.57 (d, $^3J_{HH}$ = 6.0 Hz, 3H, C*H*$_3$), 4.63 – 4.78 (m, 1H, NC*H*), 7.11 – 7.14 (m, 5H, Ar*H*), 7.19 – 7.43 (m, 20 H, Ar*H*).

^{13}C NMR ($CDCl_3$, 101.5 MHz): δ = 24.2 (t, $^3J_{CP}$ = 7.5 Hz, *C*H$_3$), 59.6 (t, $^2J_{CP}$ = 8.3 Hz, N*C*H), 126.8, 127.8, 127.9, 128.0, 128.0, 128.1, 128.5, 128.9, 132.8, 133.1, 133.3, 133.6, 144.7.

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 54.36 (br).

Elemental Analysis: $C_{32}H_{29}NP_2$ calcd (%) C 78.51, H 5.97, N 2.86, found (%) C 77.62, H 6.76, N 3.58.

MS (+ESI): 490 $[M]^+$, 416 $[M\text{-Ph}]^+$, 400 $[M\text{-(Ph + Me)}]^+$

6.2.2.6. *N,N*-bis(diphenylphosphino)-(*R*)-(+)-α-methylbenzylamine, 65

Synthesised by general method 2, using (*R*)-(+)-α-methylbenzylamine (2.5 mL, 20 mmol), diphenylphosphine chloride (2.7 mL, 15 mmol) and triethylamine (15 mL, 0.1 mol) in dichloromethane (2 x 20 mL) giving a white solid (2.1 g, mmol, 21 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.57 (d, $^3J_{HH}$ = 6.0 Hz, 3H, C*H*$_3$), 4.63 – 4.78 (m, 1H, NC*H*), 7.11 – 7.14 (m, 5H, Ar*H*), 7.19 – 7.46 (m, 20 H, Ar*H*).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 24.2 (t, $^3J_{CP}$ = 7.5 Hz, *C*H$_3$), 59.6 (t, $^2J_{CP}$ = 8.3 Hz, NCH), 126.8, 127.8, 127.9, 128.0, 128.0, 128.1, 128.5, 128.9, 132.8, 133.1, 133.3, 133.6, 144.7.

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 54.36 (br).

Elemental Analysis: $C_{32}H_{29}NP_2$ calcd (%) C 78.51, H 5.97, N 2.86, found (%) C 78.10, H 6.29, N 3.83.

MS (+ESI): 488 $[M]^+$, 384 $[M$-(PhCH(Me))$]^+$.

6.2.2.7. *N,N*-bis(diphenylphosphino)α-methylbenzylamine, 66

Synthesised by general method 2, using α-methylbenzylamine (2.5 mL, 20 mmol), diphenylphosphine chloride (2.7 mL, 15 mmol) and triethylamine (15 mL, 0.1 mol) in dichloromethane (2 x 20 mL) giving a white solid (5.4 g, 11 mmol, 55 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.57 (d, $^3J_{HH}$ = 6.0 Hz, 3H, C*H*$_3$), 4.63 – 4.78 (m, 1H, NC*H*), 7.11 – 7.15 (m, 5H, Ar*H*), 7.20 – 7.49 (m, 20 H, Ar*H*).

^{13}C NMR ($CDCl_3$, 101.5 MHz): δ = 24.21 (t, $^3J_{CP}$ = 7.5 Hz, *C*H$_3$), 59.55 (t, $^2J_{CP}$ = 8.3 Hz, NCH), 126.8, 127.8, 127.9, 128.0, 128.0, 128.1, 128.5, 128.9, 132.8, 133.1, 133.3, 133.6, 144.7.

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 54.3 (br).

Elemental Analysis: $C_{32}H_{29}NP_2$.½CH_3OH calcd (%) C 77.21, H 6.18, N 2.77, found (%) C 76.80, H 6.32, N 3.91.

MS (+ESI): 488 $[M]^+$, 384 $[M$-(PhCH(Me))$]^+$.

6.2.2.8. *N,N*-bis(di-(2,4,6-trimethyl)phenylphosphino)methylamine, 67

Synthesised by general method 3, using 1-bromo-2,4,6-trimethylbenzene (6.1 mL, 20 mmol), magnesium turnings (2.5 g, 0.10 mol), phosphorus tribromide (0.85 mL, 9.0 mmol), methylamine (2M in tetrahydrofuran, 2 mL, 4.0 mol), and triethylamine (15 mL, 0.1 mmol), giving a white solid (0.41 g, 0.73 mmol, 18 %).

Analytical data matched reported literature values:[37]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.82 – 2.13 (m, 32H, ArCH_3), 3.25 (m, 3H, NCH_3), 6.67-7.19 (m, 12H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 61.6 (s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.0 (t, $^{3}J_{CP}$ = 10.4 Hz, CH_3), 22.3 (t, J_{CP} = 7.8 Hz, CH_3), 41.2 (t, $^{2}J_{CP}$ = 9.0 Hz, NCH_3), 130.3 (s, *C*H), 134.5 – 134.6 (m, *C*H), 137.7 (s, *C*H), 140.6 – 140.8 (m, *C*P).

Elemental Analysis: $C_{37}H_{47}NP_2.CH_2Cl_2$ calcd (%) C 69.93, H 7.57, N 2.15, found (%) C 69.91, H 7.92, N 2.48.

MS (+EI): 568 $[M]^+$, 269 $[PAr_2]^+$.

N,N-bis(di-*ortho*-isopropylphenylphosphino)methylamine, **11** *N,N*-bis(di-*ortho*-trifluoro-methylphenylphosphino)methylamine, **70** were synthesised by another member of the group, using literature procedures.[98]

6.2.3. Bis(diarylphosphino)alkane Ligands

6.2.3.1. Bis(di-*ortho*-methoxyphenylphosphino)methane, 5

Synthesised by general method 1, 2-bromoanisole (1.9 mL, 15 mmol), magnesium turnings (1.5 g, 60 mmol), bis(dichlorophosphino)methane (0.60 g, 2.8 mmol) in

tetrahydrofuran (20 mL). In the work up the solvent was removed under vacuum, the resulting brown solid was redissolved in dichloromethane (40 mL) and water (40 mL) was added. A precipitate formed and good separation could not be achieved so ammonium chloride was added and the mixture was stirred for 1 h, after which separation occurred. The organic layers were collected and washed with water (2 x 20 mL). The solvent was removed and the resulting white solid was triturated cold methanol to give a white solid (1.22 g, 2.4 mmol, 86 %).

This ligand has been published, no NMR spectroscopy data has been reported.[4, 33]

^{1}H NMR ($CDCl_3$, 270 MHz): δ = 2.72 – 2.74 (m, 3H, CH_2), 3.68 (s, 12H, OCH_3), 6.69 – 6.88 (m, 8H, Ar*H*), 7.19 – 7.35 (m, 8H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = -40.4 (s).

^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 25.9 (s, CH_2), 55.5 (s, OCH_3), 110.0 (s, *C*H), 112.0 (s, *C*H), 120.9 (s, *C*H), 130.0 (s, *C*H), 132.9 (s, *C*O), 161.2.(t, J_{CP} = 7.2 Hz, *C*P).

Elemental Analysis: $C_{30}H_{33}O_4P_2$ calcd (%) C 68.84, H 5.99, found (%) C 69.51, H 5.68.

MS (+ESI): 519 $[M]^+$.

6.2.3.2. Bis(di-*ortho*-methoxyphenylphosphino)ethane, 6

Synthesised by general method 1, using 2-bromoanisole (1.6 mL, 13 mmol), magnesium turnings (2.5 g, 0.11 mmol), bis(dichlorophosphino)ethane (0.60 g, 2.6 mmol) in tetrahydrofuran (20 mL). An off white solid was produced, which was recrystalised from hot ethanol to give a white crystalline solid (0.16 g, 0.31 mmol, 12 %).

Analytical data matched reported literature values:[167]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.73 (s, 12H, OCH_3), 6.81 – 7.08 (m, 12H, Ar*H*), 7.27 – 7.32 (m, 4H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = -30.5 (s).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 20.6 – 20.7 (m, *C*H_2), 55.6 (s, O*C*H_3), 110.5 (s, *C*H), 120.6 (s, *C*H), 120.9 (s, *C*H), 130.2 (s, *C*H), 133.1 (s, *C*O), 161.6 – 161.7 (m, *C*P).

Elemental Analysis: $C_{33}H_{39}O_4P_2$ calcd (%) C 67.61, H 6.59, found (%) C 66.90, H 6.28.

MS (+ESI): 504 $[M]^+$.

Bis(di-*ortho*-methylphenylphosphino)ethane, **72** and bis(di-*ortho*-isopropylphenylphosphino)ethane, **73** were synthesised by another member of the group, using literature procedures. The syntheses of bis(di-*ortho*-ethoxyphenylphosphino)ethane, **75**, bis(di-*ortho*-isopropoxyphenylphosphino)ethane **76** and bis(di-*ortho*-(1,3-dioxolan-2-yl)-phenylphosphino)ethane, **77**, are described in Section 5.4.1.

6.3. Chapter 2 - Cotrimerisation of Ethene with Styrenic Monomers

6.3.1. General Co-Trimerisation Method

The general trimerisation method was adapted from a method reported by Wass and co-workers.[4]

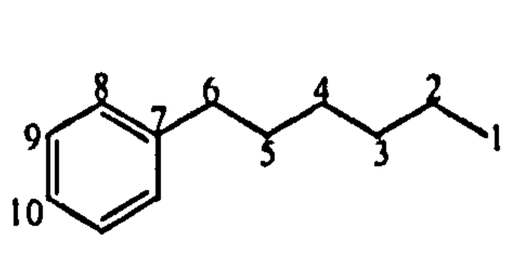
N,N-bis(di-*ortho*-methoxyphenylphosphino)methylamine, **1**, (11 mg, 20 μmol) and chromium (III) chloride tetrahydrofuran complex, $[CrCl_3(thf)_3]$, **2**, (8 mg, 20 μmol) were dissolved in tetrahydrofuran (3 mL) and stirred at room temperature in a Schlenk tube under nitrogen for 10 minutes. The solvent was removed and toluene was added (10 mL) to give a pink mixture. Methylaluminoxane (MAO, 10 % wt solution in toluene, 4 mL, 300 equivalents, 6 mmol) was then added, to give a green solution and the Schlenk tube was weighed. Next the Schlenk tube was put under an ethene (1 bar) atmosphere and styrene (30 mL) was added. The solution was vigorously stirred at room temperature for 1 h. After 1 h the ethene feed was stopped and the Schlenk tube was re-weighed. The Schlenk tube was opened to air and a dilute solution of hydrochloric acid (10 % solution) in water was slowly added to quench the reaction. The organic layer was separated and dried over magnesium sulphate, giving a colourless solution of products in toluene. A sample of the solution was analysed by GC-FID.

- The volume of toluene added depends on the volume of styrene added. Unless otherwise stated the total volume of toluene plus styrene was 40 mL, giving an overall volume of 44 mL with 4 mL of the toluene solution of MAO added.

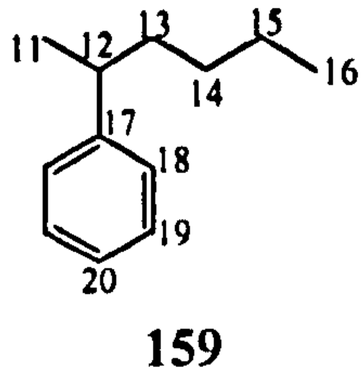
- For reactions done at high temperatures, the reaction vessel was allowed to reach temperature, then the reaction was placed under an ethene atmosphere and styrene was added.

6.3.2. Cotrimer Identification

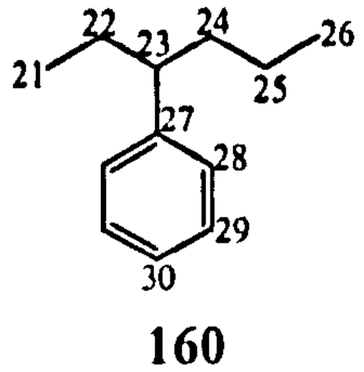
6.3.2.1. Synthesis of Standards



158



159



160

1-Phenylhexane, 158

Purchased from Sigma Aldrich

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.12 (t, J_{HH} = 7.3 Hz, 3H, CH_3), 1.25 – 1.61 (m, 6H, CH_2), 1.75 – 1.91 (m, 2H, CH_2), 2.73 – 2.86 (m, 2H, CH_2), 7.31 – 7.42 (m, 3H, Ar*H*), 7.44 – 7.52 (m, 2H, Ar*H*).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 15.7 (s, *C*H_3, C1), 24.3 (s, *C*H_2, C2), 30.7 (s, *C*H_2, C3), 33.1 (s, *C*H_2, C4), 33.4 (s, *C*H_2, C5), 37.6 (s, *C*H, C6), 127.1 (s, *C*H, C_{10}), 129.8 (s, *C*H, C9), 129.9 (s, *C*H, C8), 144.5 (s, *C*H, C7).

2-Phenylhexane, 159

Synthesised using a method reported by Black and co-workers.[94]

To a phenylmagnesium bromide (3M in diethyl ether, 8 mL, 24.0 mmol) solution in ether (40 mL) was slowly added an diethyl ether (10mL) solution of 2-hexanone (2.5 mL, 20.0 mmol) under nitrogen. After addition was complete the solution was heated under reflux overnight and a white precipitate formed. The solution was allowed to cool and dilute acid (10 % solution) was added in excess to decompose the reaction. The organic layer was separated and washed with water (2 x 20 mL). The organic layers were combines and dried over magnesium sulphate, the solvent was then

removed under vacuum. The resulting product was distilled under a static vacuum at 150 °C to give 2-phenylhexene, a clear liquid (2.9 g, 18.0 mmol, 90 %).

2-Phenylhexene (1.23 g, 7.7 mmol) was dissolved in toluene (5 mL) and an excess of palladium on carbon (5 wt % Pd on C) was added. The mixture was stirred under a hydrogen atmosphere for 2 days. The solution was filtered through celite and solvent was removed to give a clear liquid (1.1 g, 6.8 mmol, 88 %).

Analytical data matched reported literature values:[91]

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 14.2 (s, *C*H_3, C16), 22.5 (s, *C*H_3, C11), 22.9 (s, *C*H_2, C15), 30.1 (s, *C*H_2, C14), 38.3 (s, *C*H_2, C13), 40.1 (s, *C*H, C12), 127.3 (s, *C*H, C20), 129.3 (s, *C*H, C19), 129.7 (s, *C*H, C18), 147.6 (s, *C*H, C17).

3-Phenylhexane, 160

Synthesised using the same method as 2-phenylhexane, **159**, using phenylmagnesium bromide, (3M in diethyl ether, 8 mL, 24.9 mmol), diethyl ether (40 mL), 3-hexanone (2.5 mL, 20.0 mmol) under nitrogen, giving a clear liquid (2.5 g, 16.2 mmol, 81 %).

Analytical data matched reported literature values:[91]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.76 (t, J_{HH} = 7.3 Hz, 3H, C*H*$_3$), 0.83 (t, J_{HH} = 7.4 Hz, 3H, C*H*$_3$), 1.11 – 1.91 (m, 2H, C*H*$_2$), 1.48 – 1.71 (m, 4H, C*H*$_2$), 2.36 – 2.43 (m, 1H, C*H*), 7.11 – 7.18 (m, 3H, Ar*H*), 7.24 – 7.28 (m, 2H, Ar*H*).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 12.2 (s, *C*H_3, C26), 14.2 (s, *C*H_3, C21), 20.8 (s, *C*H_2, C25), 29.8 (s, *C*H_2, C22), 38.9 (s, *C*H_2, C24), 47.8 (s, *C*H, C23), 125.5 (s, *C*H, C30), 127.3 (s, 2C, *C*H, C29), 128.9 (s, 2C, *C*H, C28), 148.1 (s, *C*H, C27).

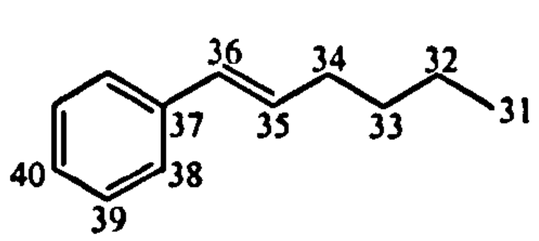
6.3.2.2. Cotrimers

Hydrogenation of Cotrimer Products

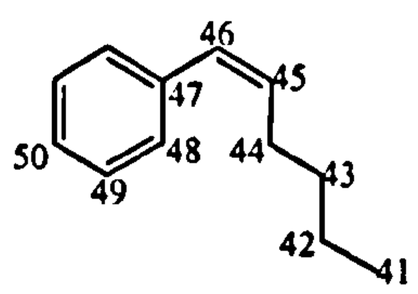
Hydrogenation of cotrimer products accomplished using method adapted from synthesis of phenylhexane described by Black and co-workers.[94] A solution of the cotrimer products (0.5 g) and palladium on carbon (0.5 g) in toluene (5 mL) was stirred at room temperature under 5 bar of H_2 for 4 days. The solution was filtered through celite to remove the palladium on carbon. The solvent was removed to give a clear yellow liquid (0.4 g, 80 %).

NMR Data of 1-Phenylhexenes from Cotrimer Products

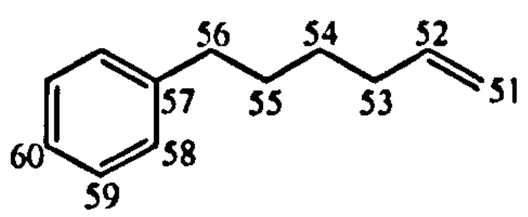
The following NMR data was produced from the cotrimers products of the cotrimerisation of styrene and ethene. NMR data found from comparison with standard samples and literature values.[92, 94]



50



51



52

MS (+EI): 160 $[M]^+$, 117 $[PhCH{=}CHCH_2]^+$, 91 $[PhCH_2]^+$.

(*E*)-1-Phenyl-1-hexene, 50

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 14.2 (s, *C*H_3, C31), 22.5 (s, *C*H_2, C32), 31.8 (s, *C*H_2, C33), 33.0 (s, *C*H_2, C34), 126.1 (s, *C*H, C38), 126.4 (s, *C*H, C40), 128.7 (s, *C*H, C39), 129.9 (s, H*C*=CH, C36), 131.3 (s, HC=*C*H, C35), 138.1 (s, *C*H, C37).

(*Z*)-1-Phenyl-1-hexene, 51

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 14.2 (s, *C*H_3, C41), 22.6 (s, *C*H_2, C42), 28.8 (s, *C*H_2, C44), 32.4 (s, *C*H_2, C43), 126.3 (s, H*C*=CH, C46), 126.6 (s, *C*H, C50), 127.9 (s, *C*H, C48), 128.4 (s, *C*H, C49), 133.4 (s, HC=*C*H, C45), 137.8 (s, *C*H, C47).

6-Phenyl-1-hexene, 52

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 28.6 (s, *C*H_2, C54), 31.2 (s, *C*H_2, C55), 33.9 (s, *C*H_2, C53), 36.0 (s, *C*H_2, C56), 113.9 (s, C=*C*H_2, C51), 125.5 (s, *C*H, C60), 128.5 (s, *C*H, C59), 128.6 (s, *C*H, C58), 139.0 (s, H*C*=CH_2, C52), 142.8 (s, *C*H, C57).

Retention Times

Table 6.1 – Retention Times of Cotrimers and Hydrogenated Cotrimers from the Cotrimerisation of Ethene and Styrene

Compound		Retention Time / min
Unhydrogenated Products	C_6	1.7
	1-Hexene	1.8
	C_{10}	8.9, 9.6, 9.8, 10.7
	3-Phenylhexene	22.2, 22.7
	6-Phenyl-1-hexene	24.7
	(*Z*)-1-Phenyl-1-hexene	25.2
	(*E*)-1-Phenyl-1-hexene	26.8
Hydrogenated Products	1-Phenylhexane	24.8
	3-Phenylhexane	22.6

Table 6.2 – Retention Time of Phenylhexane Standards

Compound	Retention Time / min
1-Phenylhexane	25.0
2-Phenylhexane	23.2
3-Phenylhexane	22.4

6.4. Chapter 3 - Trimerisation of 1,3-Dienes

6.4.1. Trimerisation of Isoprene

6.4.1.1. General Method for Trimerisation

The general trimerisation method was adapted from a method reported by Wass and co-workers.[4]

N,N-bis(di-*ortho*-methoxyphenylphosphino)methylamine (11 mg, 20 μmol) and chromium (III) chloride tetrahydrofuran complex, $[CrCl_3(thf)_3]$, (8 mg, 20 μmol) were dissolved in tetrahydrofuran (3 mL) and stirred at room temperature in a Schlenk tube under nitrogen for 10 minutes. The solvent was removed and toluene was added (10mL) to give a pink mixture. Methylaluminoxane (MAO, 10 % wt solution in toluene, 4 mL, 300 equivalents, 6 mmol) was then added, to give a green solution, isoprene (30 mL) was added and the solution was vigorously stirred at 70 °C for 1 h. The Schlenk tube was opened to air and a dilute solution of hydrochloric acid (10 % solution) in water was slowly added to quench the reaction. The organic layer was separated and dried over magnesium sulphate, giving a colourless solution of products in toluene. A sample of the solution was analysed by GC-FID.

6.4.1.2. Analysis of Products

Hydrogenation of Trimer Products

Hydrogenation of trimer products accomplished using method adapted from synthesis of phenylhexane described by Black and co-workers.[94] A solution of the trimer products (0.5 g, 2.5 mmol) and palladium on carbon (0.65 g) in toluene (5 mL) was stirred at room temperature under 5 bar of H_2 for 3 days. The solution was filtered through celite to remove the palladium on carbon. The solvent was removed to give a clear yellow liquid, which was dried under vacuum (0.4 g, 2.0 mmol, 80 %).

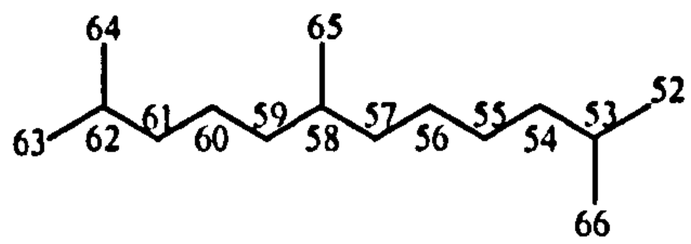
Trimer (Unhydrogenated) Products – Reaction mixture so includes linear trimers, cyclic trimers and oligomers.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.48 – 1.76 (m, 9H), 1.78 – 1.84 (m, 1H), 1.98 – 2.13 (m, 8H), 4.66 – 4.76 (m, 2H), 4.81 – 4.94 (m, 1H), 5.04 – 5.24 (m, 3H).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 16.1 – 16.3 (m), 17.6 – 18.0 (m), 18.7, 18.8, 22.5, 23.5, 23.6, 23.7, 25.7 – 26.2 (m), 26.6 – 26.9 (m), 27.2, 27.6, 28.0, 28.2, 28.3, 28.4, 28.5, 28.6, 28.7, 30.0, 30.8, 30.8, 31.3, 31.5, 31.6, 32.2, 32.3, 32.5, 35.4, 37.6, 37.7, 37.8, 38.1, 39.9, 40.2, 43.2, 48.1, 109.9, 110.0, 110.7, 111.6, 114.5, 114.6, 114.7, 122.7, 122.9, 124.1 – 124.8 (m), 125.8 – 125.5 (m), 125.8, 126.1, 126.5, 128.0, 128.1, 128.3, 129.0, 129.1, 129.5, 131.9, 132.9, 133.5, 133.7, 133.8, 134.1, 134.1, 134.8 – 135.6 (m), 136.1, 136.5, 137.2, 137.7, 141.6, 142.0, 142.1, 142.1, 145.8, 145.9.

MS (+ESI): 203 $[M]^+$, 189 $[M - CH_3]^+$, 135 $[M - CH_3C(CH_3)CHCH_2]^+$, 109 $[C_8H_{13}]^+$, 95 $[C_7H_{11}]^+$, 81 $[C_6H_9]^+$, 69 $[C_5H_9]^+$, 55 $[C_4H_7]^+$.

Hydrogenated Trimer Products – Reaction mixture, includes linear and cyclic trimer and oligomer. Only the peaks for 2,6,11-trimethyldodecane, **124** are assigned.



124

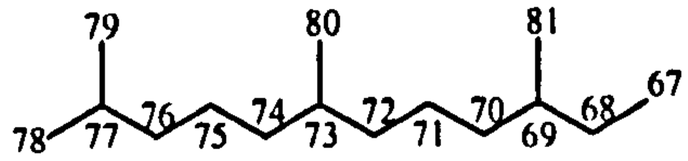
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.81 – 0.90 (m, 12H), 1.02 – 1.41 (m, 18H), 1,46 – 1.55 (m, 2H).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 19.4 – 20.0 (m, 3C, C52, C65, C66), 22.7 (C63, C64), 22.8 (C63, C64), 24.6 (C56), 24.9 (C60), 27.5, 27.6, 27.9, 28.1 (C62), 32.8 – 32.9 (m, 2H, C53, C58), 37.2 – 37.6 (m, 4H, C54, C55, C57, C59), 39.2, 39.5 (C61).

6.4.1.3. Analysis of Standards

Purchased from Sigma Aldrich.

2,6,10-Trimethyldodecane, 123



123

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.8 – 0.8 (m, 14H), 1.0 – 1.1 (m, 7H), 1.2 – 1.2 (m, 9H), 1.4-1.5 (m, 2H).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 11.3 (C67), 11.4 (C67), 19.1 (C81), 19.2 (C81), 19.6 (C80), 19.7 (C80), 22.5 (2C, C78 + C79), 22.6 (2C, C78 + C79), 24.4 (C71), 24.7 (C75), 27.9 (C77), 29.4 (C68), 29.5 (C68), 32.7 (C73), 32.8 (C73), 34.4 (C69), 36.8 (C70), 36.9 (C70), 37.2 (C74), 37.3 (C74), 37.3 (C72), 37.4 (C72), 39.3 (C76).

Trimethylcyclododecane, 128 - mixture of isomers

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.32 – 0.35 (m, 12H), 0.56 – 1.12 (m, 18H).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 17.1, 17.6, 18.1, 20.4, 20.5, 20.6, 20.9, 21.1, 21.3, 21.5, 21.9, 22.5, 22.6, 23.2, 23.7, 23.9, 24.2, 24.6, 26.6, 26.8, 27.4, 27.5, 27.8, 28.3, 28.3, 28.9, 29.7, 29.8, 29.9, 30.1, 30.2, 30.4, 30.8, 31.1, 31.5, 31.6, 31.8, 32.0, 32.2, 32.9, 33.0, 33.9, 35.7, 35.8.

Retention Times

Table 6.3 - Retention Times for Products from Trimerisation of Isoprene

	Compound	Retention Time / min
Unhydrogenated Products	Linear Trimers (C_{15}) 2,6,11-Trimethyldodecatetraene, **113**	27.6, 27.9, 28.0
	Cyclic Trimer (C_{15}) 1,5,10-Trimethylcyclododecatetrene,	29.1
	Oligomers (C_{20+})	33.2 – 37.5
Hydrogenated Products	2,6,11-Trimethyldodecane (C_{15}), **124**	26.2
	1,4,8-Trimethylcyclododecane (C_{15}),	28.1
	Oligomers (C_{20+})	36.3, 39.8

Table 6.4 – Retention Time of Alkane Standards, from Sigma Aldrich

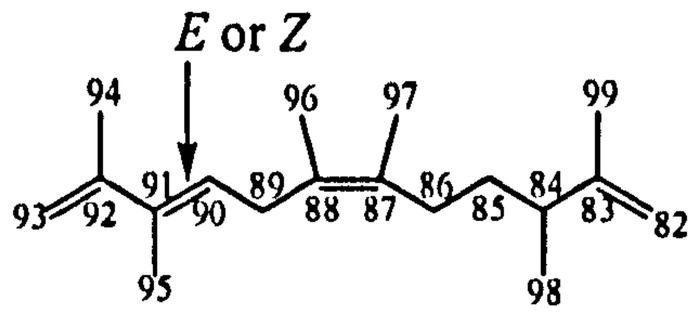
Compound	Retention Time / min
2,6,10-Trimethyldodecane, **112**	26.3
1,4,8-Trimethylcyclododecane, **128**	28.1
Trimethyldodeca-1,5-9-triene (mixture of isomers)	29.1

6.4.2. 1,3-Butadiene Polymerisation

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 25.1 – 25.2 (m), 27.5, 30.2, 32.8, 34.3, 35.6 – 35.7 (m), 38.6 – 39.2 (m), 40.1 – 41.9 (m), 43.8, 113.9 – 115.1 (m), 127.7 – 131.8 (m), 142.9 – 143.7 (m).

6.4.3. 2,3-Dimethyl-1,3-butadiene

Trimer Products



129a and 129b

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.75 – 2.10 (m, 25H), 4.55 – 5.01 (m, 5H).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 13.9 (CH_3, C98), 18.7 (CH_3), 19.1 (CH_3), 19.8 (CH_3), 21.0 (CH_3), 32.6 (CH_2), 33.6 (CH_2), 34.0 (CH_2), 41.5 (CH. C84), 109.5 (=CH, C82), 110.9 (CH_2, C93), 126.9 (C), 127.2 (HC=C, C91), 129.1 (C), 134.6 (C), 144.7 (C), 150.0 (C).

Retention Times

Table 6.5 – Retention Time of 2,3-Dimethyl-1,3-butadiene

Compound	Retention Time / min
2,3,6,7,10,11-Hexamethyldodecatetraene, **129a** and **129b**	31.4
Higher Oligomer	36.9

6.5. Chapter 4 - Chromium(I) Carbonyl Phosphine Complexes in Ethene Trimerisation

Chromium carbonyl complexes were synthesised using a method reported by Balakrishna and co-workers.[145] The syntheses in this section have been published.[160]

6.5.1. Chromium Carbonyl Phosphine Complexes

6.5.1.1. $[Cr(CO)_4(1)]$, 133

Chromium hexacarbonyl, $[Cr(CO)_6]$, (0.3 g, 1.4 mmol) and *N,N*-bis(di-*ortho*-methoxyphenylphosphino)methylamine, **1**, (0.5 g, 0.96 mmol) were mixed in toluene (40 mL) under nitrogen. The mixture was heated under reflux for 72 h. The solution was cooled to 0 °C and filtered under nitrogen via a cannula, to remove excess $[Cr(CO)_6]$. Solvent was removed and the product extracted into dichloromethane (10 mL) and filtered again. To this solution was added methanol (20 mL) to precipitate the product, giving a yellow solid (380 mg, 0.56 mmol, 56 %).

Analytical data matched reported literature values:[40]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.42 (s, 3H, C*H*$_3$), 3.59 (s, 12H, OC*H*$_3$), 6.83 – 6.88 (m, 8H, Ar*H*), 7.06 – 7.10 (m, 4H, Ar*H*), 7.24 – 7.32 (m, 4H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 102 (s).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 37.6 (s, *C*H$_3$), 55.0 (s, OCH$_3$), 110.7 (s, *C*H), 120.0 (t, J_{CP} = 5.5 Hz, *C*H), 131.6 (s, *C*H), 129.8 (t, *C*H), 133.1 (t, J_{CP} = 11.0 Hz), 159.7 (s, *C*P).

IR (CH_2Cl_2): ν = 1869.4 (C≡O), 1887.8 (C≡O), 1907.0 (C≡O), 2002.7 (C≡O) cm^{-1}.

Elemental Analysis: $C_{33}H_{31}CrNO_8P_2.½CH_2Cl_2$ calcd (%) C 55.95, H 4.45, N 1.93, found (%) C 55.17, H 4.85, N 1.88.

MS (+EI): 683 $[M]^+$, 571 $[M\text{-}4CO]^+$, 519 $[1]^+$.

6.5.1.2. $[Cr(CO)_4(19)]$, 134

Synthesised using the same method as $[Cr(CO)_4(1)]$, with chromium hexacarbonyl, $[Cr(CO)_6]$, (350 mg, 1.6 mmol) and *N,N*-bis(diphenylphosphino)isopropylamine, **19** (500 mg, 1.2 mmol) in toluene (40 mL) under nitrogen, giving a yellow solid (0.29 g, 0.46 mmol, 44 %).

Analytical data matched reported literature values:[145]

^1H NMR ($CDCl_3$, 300 MHz): δ = 0.62 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3), 3.51 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, C*H*), 7.19 – 7.90 (m, 20H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 114.0 (s).

^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 1.1 (s, *C*H_3), 23.6 (s, *C*H), 128.1 (d, J_{CP} = 5.5 Hz, *C*H), 128.5 (s, J_{CP} = 5.5 Hz, *C*H), 130.6 (s, *C*H), 132.0 (t, J_{CP} = 15.9 Hz, *C*H), 132.9 (d, J_{CP} = 21.9 Hz, *C*H), 127.1 – 127.2 (m, *C*P).

IR (CH_2Cl_2): ν = 1888.7 (C≡O), 1918.7 (C≡O), 2005.6 (C≡O), 2988.2, 3070.6 cm^{-1}.

Elemental Analysis: $C_{31}H_{27}CrNO_8P_2$ calcd (%) C 62.95, H 4.60, N 2.37, found (%) C 62.60, H 4.62, N 1.90.

MS (+EI): 591 $[M]^+$, 507 $[M\text{-}3CO]^+$.

6.5.1.3. $[Cr(CO)_4(5)]$, 135

Synthesised using the same method as $[Cr(CO)_4(1)]$, using chromium hexacarbonyl, $[Cr(CO)_6]$, (0.17 mg, 0.60 mmol) and bis(di-*ortho*-methoxyphenylphosphino)methane, **5**, (0.3 mg, 0.77 mmol) were mixed in toluene (40 mL) under nitrogen, giving a yellow solid (120 mg, 0.17 mmol, 28 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.33 (s, 2H, CH_2), 3.56 (s, 12H, OCH_3), 6.65 – 6.78 (m, 4H, Ar*H*), 6.85 – 6.95 (m, 4H, Ar*H*), 7.05 – 7.28 (m, 8H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 19.9 (s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.8 (s, CH_3), 55.1 (s, OCH_3), 110.6 (s, *C*H), 120.1 (t, J_{CP} = 5.4 Hz, *C*H), 128.2, 129.0, 131.5 (s, *C*H), 133.7 (t, J_{CP} = 6.88 Hz, *C*O), 160.2.(t, J_{CP} = 10.2 Hz, *C*P).

IR (CH_2Cl_2): ν = 1860.9 (C≡O), 1888.0 (C≡O), 1906.1 (C≡O), 2001.7 (C≡O) cm^{-1};.

Elemental Analysis: $C_{33}H_{30}CrO_8P_2$ calcd (%) C 59.09, H 4.52, found (%) C 59.81, H 4.11.

6.5.1.4. [Cr(CO)$_4$(NO)(1)], 136

[Cr(CO)$_4$(1)], **133** (140 mg, 0.20 mmol) and [NO][BF_4] (50 mg, 0.40 mmol) were dissolved in a toluene/methanol mix (10 mL, 1 mL, 10:1) under nitrogen to give a yellow solution with a yellow precipitate. The solution was stirred at room temperature for 30 min, after which the precipitate had dissolved. The solution was stirred for a further 30 min and was monitored by infra-red spectroscopy. The solution was filtered and reduced to about 5 mL. To this was added diethyl ether (20 mL) to give a yellow precipitate, which was isolated by filtration and dried under vacuum (73 mg, 0.095 mmol, 47 %). X-ray crystals were formed from dichloromethane and hexane at -5 °C.

IR (CH_2Cl_2): ν = 1754.8 (N≡O), 2024.4 (C≡O), 2090.8 (C≡O) cm^{-1};

Elemental Analysis: $C_{33}H_{31}BCrF_4N_2O_8P_2$ calcd (%) C 49.76, H 4.05, N 3.63, found (%) C 49.83, H 4.45, N 4.79.

6.5.1.5. [Cr(CO)$_4$(NO)(19)], 137

Synthesised using the same method as [Cr(CO)$_4$(1)], using [Cr(CO)$_4$(19)], **134** (72 mg, 0.15 mmol) and [NO][BF_4] (30 mg, 0.26 mmol) in a toluene/methanol mix (10 mL, 1 mL, 10:1) under nitrogen, to give a yellow solid (35 mg, 0.061 mmol, 41 %).

IR (CH_2Cl_2): ν = 1759.5 (N≡O), 2021.8 (C≡O), 2092.3 (C≡O) cm^{-1};

6.5.2. Oxidation of Complexes 133 and 134 with Acetyl Ferrocinium Tetrafluoroborate

6.5.2.1. [Cr(CO)$_4$(1)][BF_4], 138

[Cr(CO)$_4$(1)], **133** (20 mg, 0.029.mmol) and acetyl ferrocinium tetrafluoroborate, (12 mg, 0.036 mmol) were dissolved in dichloromethane (5 mL) under nitrogen to give a dark purple solution. The Schlenk tube was covered with foil to reduce exposure of the reaction mixture to light. The solution was stirred at room temperature for 2 h and was monitored by infra-red spectroscopy. Diethyl ether (20 mL) was added and a black solid precipitated out which decomposed on isolation.

IR (CH_2Cl_2): ν = 1965.3 (C≡O), 2026.1 (C≡O), 2082.9 (C≡O) cm^{-1};

6.5.2.2. [Cr(CO)$_4$(19)][BF_4], 139

Synthesised using the same method as [Cr(CO)$_4$(**1**)][BF_4], **138** using [Cr(CO)$_4$(**18**)], **134** (20 mg, 0.034.mmol) and acetyl ferrocinium tetrafluoroborate, (15 mg, 0.045 mmol) in dichloromethane (5 mL) under nitrogen. After monitoring with IR spectroscopy diethyl ether (20 mL) was added and a black solid precipitated out which decomposed on isolation.

IR (CH_2Cl_2): ν = 1962.9 (C≡O), 2033.4 (C≡O), 2086.6 (C≡O) cm^{-1}.

6.5.3. Reactions of Complexes 133, 134, 135 with Amine Oxides

General Method

The trimethylamine-*N*-oxide was purified by sublimation. Complex **133** (20 mg, 0.03 mmol) and acetyl ferrocinium tetrafluoroborate (12 mg, 0.035 mmol) were dissolved with stirring in toluene (10 mL), giving a purple solution of **138**, as confirmed by IR spectroscopy. To this solution was slowly added a solution of trimethylamine-*N*-oxide (38 mg, 0.5 mmol) in toluene (5 mL). The solution was stirred at room temperature for 2 h, after which IR spectroscopy showed only complexes **138** and trace amounts of **133**. The mixture was heated under reflux for 16 h but again IR spectroscopy showed almost equal amounts of **133** and **138**, showing decomposition of **138** but no removal of CO ligands.

This synthesis was attempted with complexes **134** and **135** and as with complex **133**, there was no evidence of the removal of CO ligands. Pyridine-*N*-oxide was also used as the amine oxide and again there was no evidence of CO removal, only decomposition of the oxidised complex.

6.5.4. Reactions of 133, 134, 135 with Triethylaluminium ($AlEt_3$)

General Method

Complex **133** (20 mg, 0.03 mmol) and acetyl ferrocinium tetrafluoroborate (12 mg, 0.035 mmol) were dissolved with stirring in toluene (10 mL), giving a purple solution of **138**, as confirmed by IR spectroscopy. To this solution was added trimethyl aluminium in toluene (1.9 M, 4.7 mL, 9 mmol), the solution immediately turned orange/brown. The solution was stirred for 10 min at room temperature. IR spectroscopy indicated no peaks in the CO region.

This synthesis was attempted with complexes **134** and **135** and as with complex **133**, IR spectroscopy indicated no peaks in the CO region.

6.5.5. Ethene Oligomerisation Methods

6.5.5.1. At Low Ethene Pressure

The amine oxide, trimethyl-*N*-oxide (TMNO), was activated and purified by sublimation. Complex **133** (20 mg, 0.03 mmol) and acetyl ferrocinium tetrafluoroborate (12 mg, 0.035 mmol) were dissolved with stirring in toluene (10 mL), giving a purple solution of **138**. To this was added a solution of trimethylamine-*N*-oxide (38 mg, 0.5 mmol) in toluene (5 mL). The solution was degassed and placed under an ethene atmosphere (1 bar). The solution was stirred at 70 °C for 2 h. After 2 h the solution was allowed to cool to room temperature and dilute hydrochloric acid (10 % solution) was added to quench the reaction. The organic layers were collected, washed with distilled water (2 x 10 mL) and dried over magnesium sulphate. The GC trace showed no oligomerisation products. The same method was used for complexes **134** and **135**.

6.5.5.2. At High Ethene Pressure without Triethylaluminium

Complex **133** (20 mg, 0.03 mmol) and acetyl ferrocinium tetrafluoroborate (12 mg, 0.035 mmol) were loaded into a reaction cell in a Baskerville 10 multicell autoclave in an inert atmosphere glove box. The autoclave was removed from the glove box and toluene (4 mL) was added. To each cell was added a solution of freshly sublimed trimethylamine-*N*-oxide (38 mg, 0.5 mmol) in toluene (1.5 mL) *via* syringe. The autoclave was closed, heated to 60 °C and placed under 40 bar of ethene. The reaction was stirred for 1 h, after which the reactor was allowed to cool to room temperature and the pressure was slowly released. Dilute hydrochloric acid (10 % solution) was added to each cell to quench the reaction. The organic layer was collected, washed with distilled water (2 x 5 mL) and then dried over magnesium sulphate. The GC trace showed no oligomerisation products. The same method was used for complexes **134** and **135**.

6.5.5.3. At High Ethene Pressure with Triethylaluminium

Complex **133** (20 mg, 0.03 mmol) and acetyl ferrocinium tetrafluoroborate (12 mg, 0.035 mmol) were loaded into a reaction cell in a Baskerville 10 multicell autoclave in

an inert atmosphere glove box. The autoclave was removed from the glove box and toluene (1.3 mL) was added. To each cell was added triethylaluminium (1.9M toluene solution, 9.0 mmol, 4.7 mL) *via* syringe. The autoclave was closed, heated to 60 °C and placed under 40 bar of ethene. The reaction was stirred for 1 h, after which the reactor was allowed to cool to room temperature and the pressure was slowly released. Dilute hydrochloric acid (10 % solution) was added to each cell to quench the reaction. The organic layer was collected, washed with distilled water (2 x 5 mL) and then dried over magnesium sulphate. The GC trace showed no oligomerisation products. The same method was used for complexes **134** and **135**.

6.6. Chapter 5 - Phosphine Ligands for Ethene Trimerisation

6.6.1. Synthesis of Ligands

6.6.1.1. *N,N*-bis-*ortho*-ethoxyphenylphosphino)methylamine, 68

(a) Preparation of 1-Bromo-2-ethoxybenzene, **148**

2-Bromoethoxybenzene, **148**, was synthesised using a method reported by Reitz and co-workers.[165]

A mixture of 2-Bromophenol (4 mL, 34.4 mmol), bromoethane (5.4 mL, 71.4 mmol) and potassium carbonate (9.6 g, 69.4 mmol) were in dimethylforamide (20 mL) was heated at reflux overnight. The mixture was allowed to warm to room temperature and water (30 mL) was added and the product was extracted into toluene (3 x 20 mL). The organic layers were combined, washed with water (2 x 20 mL) and dried over magnesium sulphate. Finally the solvent was removed to give a clear liquid. The crude product was used in the next stage without further purification (6.58 g, 32.7 mmol, 95 %)

Analytical data matched reported literature values:[165]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.48 (t, $^{3}J_{HH}$ = 8.0 Hz, 3H, CH_3), 4.11 (q, $^{3}J_{HH}$ = 8.0 Hz, 2H, CH_2), 6.83 (td, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 4.0 Hz, 4H, Ar*H*), 6.89 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{2}J_{HH}$ = 2.0 Hz, 4H, Ar*H*), 7.25 (td, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 2.0 Hz, 4H, Ar*H*), 7.54 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 2.0 Hz, 4H, Ar*H*).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 28.5 (s, *C*H_3), 67.9 (s, O*C*H_2), 112.5 (s, *C*H), 114.3 (s, *C*H), 122.7 (s, *C*H), 128.5 (s, *C*H), 133.6 (s, *C*O), 155.1 (s, *C*Br).

MS (EI): 200 $[M]^+$, 172 $[M\text{-}(CH_2CH_3)]^+$.

(b) Preparation of *N,N*-bis(di-*ortho*-ethoxyphenylphosphino)methylamine, 68

Synthesised by general method 1, using 1-bromo-2-ethoxybenzene, 148 (3.3 g, 16.4 mmol), magnesium turnings (1.25 g, 0.10 mol), *N,N*-bis(dichlorophosphino)methylamine (0.51 g, 2.2 mmol) and tetrahydrofuran (10 + 20 + 20 mL). The workup of the final product was: First cold methanol (5 mL) was added to decompose the Grignard reagent and was removed under vacuum. The resulting yellow solid was dissolved in dichloromethane and filtered, to remove the magnesium chloride salt. Diethyl ether (10 mL) was added, the mixture was stirred for 1 h and then filtered. Finally the product was triturated with cold methanol to give a white solid (1.14 g, 2.0 mmol, 90 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.91 (t, $^{3}J_{HH}$ = 7.0 Hz, 12H, CH_2CH_3), 2.49 (t, $^{3}J_{HP}$ = 2.6 Hz, 3H, NCH_3), 3.80 – 3.91 (m, 8H, CH_2), 6.79 – 6.87 (m, 8H, Ar*H*), 7.05 -7.14 (m, 4H, Ar*H*), 7.28 – 7.33 (m, 4H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 56.3 (s).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 14.1 (s, CH_2CH_3), 33.8 (t, $^{2}J_{CP}$ = 5.4 Hz, NCH_3), 55.1 (s, OCH_2), 110.8 (s, *C*H), 119.8 (s, *C*H), 129.6 (s, *C*H) 133.2 (t, $^{3}J_{CP}$ = 3.1 Hz, *C*O), 160.6 (t, $^{1}J_{CP}$ = 8.1 Hz, *C*P).

Elemental Analysis: $C_{33}H_{39}NO_4P_2.CH_3OH$ calcd (%) C 67.20, H 7.13, N 2.31, found (%) C 66.99, H 7.06, N 2.96.

MS (+ESI): 576 $[M]^+$, 598 $[M + Na]^+$.

6.6.1.2. *N,N*-Bis-(di-*ortho*-(1,3-dioxolan-2-yl)phenylphosphino)methylamine, 69

Synthesised by general method 1, using 2-(2-bromophenyl)-1,3-dioxolane, **151** (1.4 mL, 10 mmol), magnesium turnings (2.5 g, 0.11 mmol), *N,N*-bis(dichlorophosphino)methylamine (0.5 g, 2.1 mmol) in tetrahydrofuran (20 mL). An off white solid was produced (0.99 g, 1.4 mmol, 68 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.54 (t, $^{3}J_{HP}$ = 2.7 Hz, 3H, NCH_3), 3.65 – 3.77 (m, 8H, CH_2), 3.87 – 3.93 (m, 8H, CH_2), 6.02 (t, $^{3}J_{HH}$ = 2.0 Hz, 4H, C*H*), 7.16 – 7.18 (m, 4H, Ar*H*), 7.24 – 7.28 (m, 4H, Ar*H*), 7.36 – 7.40 (m, 4H, Ar*H*), 7.63 – 7.67 (m, 4H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 53.9 (s).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 33.2 – 33.3 (m, NCH_3), 65.0 (s, OCH_2CH_2O), 65.2 (s, OCH_2CH_2O), 101.3 (t, J_{CP} = 11.2 Hz, *C*H)), 126.9 (t, J_{CP} = 2.3 Hz, *C*H), 128.7 (s, *C*H), 129.1 (s, *C*H), 133.1 (s, *C*H), 137.8 (t, J_{CP} = 6.9 Hz, *C*C), 139.9 (t, J_{CP} = 10.8 Hz, *C*P).

Elemental Analysis: $C_{37}H_{39}NO_8P_2.CH_3OH$ calcd (%) C 63.42, H 6.02, N 1.95, found (%) C 62.55, H 5.83, N 2.19.

MS (+ESI): 688 $[M]^+$, 710 $[M + Na]^+$.

6.6.1.3. Bis(di-*ortho*-ethoxyphenylphosphino)ethane, 75

Synthesised by general method 1, using 1-bromo-2-ethoxybenzene, **148** (see synthesis of *N,N*-bis-*ortho*-ethoxyphenylphosphino)methylamine, **68** for synthesis of 1-bromo-2-ethoxybenzene) (4.0 g, 20.0 mmol), magnesium turnings (2.5 g, 0.11 mmol), bis(dichlorophosphino)-ethane (0.93 g, 4.0 mmol) in tetrahydrofuran (20 mL). An off white solid was produced (90 mg, 0.16 mmol, 4 %).

Analytical data matched reported literature values:[173]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.16 (t, $^{3}J_{HH}$ = 7.0 Hz, 12H, CH_3), 2.36 (br s, 4H, CH_2CH_2), 3.87 – 3.94 (m, 8H, OCH_2), 6.73 – 6.95 (m, 12H, Ar*H*), 7.23 – 7.36 (m, 4H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = -23.1 (s).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 14.5 (s, CH_2CH_3), 48.5 – 48.7 (m, NCH_3), 63.7 – 63.8 (m, OCH_2), 69.52 (s, *C*H), 111.1 (s, *C*H), 120.5 (s, *C*H), 130.1 (s, *C*H), 133.5 – 134.8 (m, *C*H, *C*O), 160.7 – 160.9 (m, *C*P).

Elemental Analysis: $C_{34}H_{40}O_4P_2.CH_3OH$ calcd (%) C 69.29, 7.31, found (%) C 69.07, H 7.06.

MS (+ESI): 575 $[M]^+$, 597 $[M + Na]^+$.

6.6.1.4. Bis(di-*ortho*-isopropxyphenylphosphino)ethane, 76

(a) Preparation of 1-Bromo-2-isopropoxybenzene, 149

Synthesised using the same method as for 1-bromo-2-ethoxybenzene, 148, using 2-bromophenol (5.0 mL, 43.0 mmol), isopropylbromide (9.4 mL, 0.1 mol) and potassium carbonate (13.8 g, 0.1 mol) in dimethylforamide (40 mL) to give a clear liquid (7.47 g, 34.8 mmol, 81 %).

Analytical data matched reported literature values:[165]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.19 (d, $^3J_{HH}$ = 4.0 Hz, 6H, C*H*$_3$), 4.19 (sept, $^3J_{HH}$ = 4.0 Hz, 12H, C*H*), 6.61 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 7.01 (dt, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar*H*), 7.56 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar*H*).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 22.3 (s, *C*H$_3$), 71.9 (s, *C*H), 114.5 (s, *C*Br), 115.8 (s, *C*H), 122.3 (s, *C*H), 128.2 (s, *C*H), 134.3 (s, *C*H), 155.4 (s, *C*O).

Elemental Analysis: $C_9H_{11}BrO$ calcd (%) C 50.26, H 5.15, found (%) C 50.62, H 5.48.

MS (+EI): 216 [*M*], 171 [*M*-(CH(CH$_3$)$_2$)].

(b) Preparation of bis(di-*ortho*-isopropoxyphenylphosphino)ethane, 76

Synthesised by general method 1, using 1-bromo-2-isopropoxybenzene, 149 (1.55 g, 7.2 mmol), magnesium turnings (2.5 g, 0.11 mmol), bis(dichlorophosphino)ethane

(0.28 g, 1.2 mmol) in tetrahydrofuran (20 mL). A white solid was produced (0.51 g, 0.81 mmol, 68 %)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.05 (dd, J_{HH} = 8.0 Hz, J_{HH} = 24.0 Hz 6H, CH_3), 2.24 (br, 4H, CH_2CH_2), 4.45 (sept, J_{HH} = 8.0 Hz, 1H, C*H*), 6.74 – 6.84 (m, 8H, Ar*H*), 7.19 – 7.29 (m, 8H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = -24.1 (s).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 21.6 (s, *C*H_3), 21.7 (s, *C*H_3), 47.1 (d, J_{CP} = 15.1 Hz, *C*H_2*C*H_2), 69.5 (s, *C*H), 112.0 (s, *C*H), 120.0 (s, *C*H), 129.3 (s, *C*H), 134.1 (m, *C*H, *C*O), 159.5 – 159.6 (m, *C*P).

Elemental Analysis: $C_{38}H_{48}O_4P_2.CH_3OH$ calcd (%) C 70.68, H 7.91, found (%) C 71.33, H 7.78.

MS (+ESI): 631 $[M]^+$, 653 $[M + Na]^+$.

6.6.1.5. Bis(di-*ortho*-(1,3-dioxolan-2-yl)phenylphosphino)ethane, 77

Synthesised by general method 1, using 2-(2-bromophenyl)-1,3-dioxolane, **151** (1.4 mL, 10 mmol), magnesium turnings (2.5 g, 0.11 mmol), *N,N*-bis(dichlorophosphino)methylamine (0.5 g, 2.2 mmol) in tetrahydrofuran (20 mL). An off white solid was produced (0.62 g, 0.89 mmol, 40 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.16 (t, $^{3}J_{HP}$ = 4.0 Hz, 4H, CH_2CH_2), 3.91 – 3.99 (m, 8H, OCH_2CH_2O), 4.01 – 4.08 (m, 8H, OCH_2CH_2O), 6.37 – 6.40 (m, 4H, C*H*), 7.18 – 7.26 (m, 8H, Ar*H*), 7.33 – 7.39 (m, 4H, Ar*H*), 7.60 – 7.63 (m, 4H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = -38.0 (s).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 23.9 (d, $^2J_{CP}$ = 5.1 Hz, CH_3), 65.1 (d, J_{CP} = 22.1 Hz, OCH_2CH_2O), 101.5 (t, J_{CP} = 12.1 Hz, OCHO), 126.3 (m, *C*H), 128.9 (s, *C*H), 129.3 (s, *C*H), 131.9 (s, *C*H), 137.2 (m, *C*C), 141.3 (t, J_{CP} = 10.1 Hz, *C*P).

Elemental Analysis: $C_{38}H_{40}O_8P_2.CH_2Cl_2$ calcd (%) C 60.71, H 5.49, found (%) C 61.48, H 5.75.

MS (+ESI): 687 $[M]^+$, 709 $[M + Na]^+$.

6.6.2. Unsuccessful Ligands Syntheses

6.6.2.1. Synthesis of *N,N*-bis(di-*ortho*-isopropoxyphenylphosphino)methyl-amine, 146

Synthesised by general method 1, using 1-bromo-2-isopropoxybenzene, 149 (1.1 g, 5.0 mmol), magnesium turnings (0.5 g, 20.8 mmol), *N,N*-bis(dichlorophosphino)methyl-amine (0.25 g, 1.1 mmol) and tetrahydrofuran (20 mL). Synthesis of the PNP ligand was unsuccessful.

6.6.2.2. *N,N*-bis(di(2,3-dihydrobenzofuran)phosphino)methylamine, 147

(a) Synthesis of 1,3-Dibromo-2-(2-bromoethoxy)benzene

Synthesis using a method reported by Kerrigan and Coworkers[166] 1,2-Dimbromophenol (0.52 mL, 6.0 mmol) was added to a stirred solution of sodium hydroxide (0.25 g, 6.3 mmol) in distilled water (20 mL). The solution was stirred under reflux overnight. The reaction was allowed to cool to room temperature and the product was extracted into ether (2 x 20 mL). The organic layers were combined and washed with 1 M aqueous sodium hydroxide (50 mL) and brine (50 mL), dried over magnesium sulphate and finally solvent was removed to give a clear liquid. The crude product was dried under vacuum overnight and used in the next stage without further purification (2.0 g, 5.5 mmol, 91 %)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.75 (t, $^{3}J_{HH}$ = 6.0 Hz, 2H, OCH_2CH_2Br), 4.33 (t, $^{3}J_{HH}$ = 6.0 Hz, 2H, OCH_2CH_2Br), 6.73 (t, $^{3}J_{HH}$ = 8.0 Hz, 2H Ar*H*), 7.12 – 7.14 (m, 1H Ar*H*), 7.26 – 7.28 (m, 1H Ar*H*).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 30.1 (CH_2Br), 72.4 (OCH_2), 118.3 (*C*H), 126.7 (*C*H), 132.8 (*C*H), 151.3 (*C*H).

(b) Synthesis of 7-Bromo-2,3-dihydrobenzofuran, **150**

n-Butyl-lithium (1.6 M in hexanes, 4.5 mL, 7.3 mmol) was added to a solution of 1,3-dibromo-2-(2-bromoethoxy)benzene under nitrogen at -78 °C, in a mixture of tetrahydrofuran (25 mL) and hexane (5 mL). The mixture was stirred at this temperature for 30 mins, allowed to warm to 0 °C and poured onto distilled water (50 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (2 x 50 mL). The organic layers were combined and dried over magnesium sulphate. The solvent was then removed and the resulting yellow oil was dried under vacuum (2.13 g, 10.7 mmol, 94 %).

Analytical data matched reported literature values:[166]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.33 (t, $^{3}J_{HH}$ = 8.0 Hz, 2H, OCH_2CH_2), 4.67 (t, $^{3}J_{HH}$ = 6.0 Hz, 2H, OCH_2CH_2), 6.37 – 6.40 (m, 4H, C*H*), 6.90 (t, $^{3}J_{HH}$ = 8.0 Hz, 2H Ar*H*), 6.90 (d, $^{3}J_{HH}$ = 6.0 Hz, 1H Ar*H*).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 30.6, 71.4, 121.8, 123.9, 128.3, 131.0, 132.8, 157.3.

MS (+ESI): 198 $[M]^+$.

(c) Synthesis of *N*,*N*-bis(di(2,3-dihydrobenzofuran)phosphino)methylamine, **147**

Synthesised by general method 1, using 7-bromo-2,3-dihydrobenzofuran, **150** (1.0 g. 5.0 mmol), magnesium turnings (2.5 g, 0.10 mol), *N*,*N*-bis(dichlorophosphino)methylamine (0.25 g, 1.1 mmol) and tetrahydrofuran (20 mL). Synthesis of the PNP ligand was unsuccessful.

6.6.2.3. Synthesis of Bis(di(2,3-dihydrobenzofuran)phosphino)ethane

Synthesised by general method 1, using 7-bromo-2,3-dihydrobenzofuran, **150**, (1.0 g. 5.0 mmol), magnesium turnings (2.5 g, 0.10 mol), bis(dichlorophosphino)ethane (0.25 g, 1.1 mmol) and tetrahydrofuran (20 mL). Synthesis of the ligand was unsuccessful as decomposition occurred.

6.6.3. Chromium Carbonyl PNP Complexes, $[Cr(CO)_4(PNP)]$

6.6.3.1. $[Cr(CO)_4(68)]$, 153

Synthesised using the same method as $[Cr(CO)_4(1)]$, **133**, using chromium hexacarbonyl, $[Cr(CO)_6]$, (0.2 g, 0.91 mmol) and *N,N*-bis(di-*ortho*-ethoxyphenyl-phosphino)methylamine, **68** (0.1 g, 0.17 mmol) in toluene (20 mL) under nitrogen, giving a yellow/green solid (54 mg, 0.07 mmol, 40 %). X-ray crystals were formed from slow diffusion of methanol into a dichloromethane solution of the complex.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.67 (t, $^{3}J_{HH}$ = 7.0 Hz, 12H, CH_2CH_3), 2.97 (t, $^{3}J_{HH}$ = 8.5 Hz, 3H, NCH_3), 3.60 – 3.68 (m, 8H, OCH_2), 6.73 (dd, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 1.8 Hz, 4H, Ar*H*), 6.98 (t, $^{3}J_{HH}$ = 6.7 Hz, 4H, Ar*H*), 7.33 (t, $^{3}J_{HH}$ = 7.8 Hz, 4H, Ar*H*), 7.62 – 7.73 (m, 4H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 103.8 (s).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.6 (s, CH_3), 32.3 – 32.4 (m, NCH_3), 63.1 (s, OCH_2), 110.5 (s, *C*H), 120.4, 131.2 (s, *C*H), 157.9 – 159.1 (m, *C*P).

IR (CH_2Cl_2): ν = 1884.6 (b, C≡O), 1908.2 (sh, C≡O), 2001.9 (s, C≡O) cm^{-1}.

Elemental Analysis: $C_{37}H_{39}CrNO_8P_2.CH_2Cl_2$ calcd (%) C 55.35, H 5.01, N 1.70, found (%) C 55.70, H 5.07, N 2.21.

MS (+ESI): 762 $[M + Na]^+$, 734 $[M\text{-CO}, + Na]^+$, 598 $[68 + Na]^+$, 576 $[68]^+$.

6.6.3.2. [Cr(CO)$_4$(75)], 154

Synthesised using the same method as [Cr(CO)$_4$(1)], with chromium hexacarbonyl, [Cr(CO)$_6$], (60 mg, 0.27 mmol) and bis(di-*ortho*-ethoxyphenylphosphino)ethane, **75** (40 mg, 0.069 mmol) in toluene (10 mL) under nitrogen, giving a yellow/green solid (24 mg, 0.033 mmol, 47 %). X-ray crystals were formed from slow diffusion of methanol into a dichloromethane solution of the complex.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.66 (t, $^3J_{HH}$ = 8.0 Hz, 12H, CH_3), 2.74 – 2.96 (m, 4H, CH_2CH_2), 3.70 – 3.81 (m, 8H, OCH_2), 6.68 – 6.73 (m, 4H, Ar*H*), 6.87 – 7.04 (m, 4H, Ar*H*) 7.23 – 7.36 (m, 4H, Ar*H*), 7.62 – 7.74 (m, 4H, Ar*H*).

^{31}P NMR ($CDCl_3$, ref-H_3PO_4, 121 MHz): δ = 76.3 (s).

^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 14.1 (s, *C*H$_3$), 30.9 – 31.0 (m, NCH$_3$), 63.4 (s, OCH$_2$), 111.2 (s, *C*H), 119.9 (s, *C*H), 120.0 (s, *C*H), 130.7 (t, *C*H), 131.2 (s, CO), 159.1 – 159.2 (m, *C*P).

IR (CH_2Cl_2): ν = 1870.0 (sh, C≡O), 1887.8 (br, C≡O), 1905.0 (sh, C≡O), 2001.9 (s, C≡O) cm^{-1}.

Elemental Analysis: $C_{38}H_{40}CrO_8P_2$ calcd (%) C 61.79, H 5.46, found (%) C 62.64, H 5.75.

MS (+ESI): 761 [*M* + Na]$^+$, 738 [*M*]$^+$, 575 [**75**]$^+$.

6.6.4. Platinum Chloride PNP Complexes – [PtCl$_2$(PNP)]

Platinum chloride PNP complexes were synthesised using a method reported by Gallo and co-workers.[164]

6.6.4.1. $[PtCl_2(69)]$, 155

To a dichloromethane (5 mL) solution of *N,N*-bis-(di-*ortho*-(1,3-dioxolan-2-yl)-phenylphosphino)methylamine, **69** (40 mg, 0.058 mmol) was added a dichloromethane (5 mL) solution of $[PtCl_2(COD)]$ (22 mg 0.058 mmol) under nitrogen, giving a clear solution. The solution was stirred for 2 h, after which solvent was removed and the resulting off white solid was washed with ether (2 x 10 mL) and dried under vacuum, giving a white solid (45 mg, 0.047 mmol, 81 %).

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.77 (t, $^3J_{HP}$ = 11.6 Hz, 3H, CH_3), 3.38 – 3.50 (m, 8H, OCH_2CH_2O), 3.79 – 3.89 (m, 8H, OCH_2CH_2O), 7.37 – 7.60 (m, 4H, Ar*H*), 7.73 – 7.80 (m, 12H, Ar*H*).

^{31}P NMR (DMSO-d_6, ref-H_3PO_4, 121 MHz): δ = 16.2 (s, J_{PPt} = 3340 Hz).

Elemental Analysis: $C_{37}H_{39}Cl_2NO_8P_2Pt$ calcd (%) C 46.60, H 4.12, N 1.47 found (%) C 47.09, H 4.84, N 1.85.

MS (+ESI): 976 $[M + Na]^+$, 918 $[M - Cl]^+$.

6.6.4.2. $[PtCl_2(76)]$, 156

Synthesised using the same method as $[PtCl_2(69)]$, **155** with bis(di-*ortho*-isopropoxyphenyl)ethane, **76** (40 mg, 0.058 mmol) and $[PtCl_2(COD)]$ (24 mg, 0.058 mmol) in dichloromethane (10 mL), giving a white solid (48 mg, 0.054 mmol, 84 %). X-ray crystals were formed from slow diffusion of dimethylforamide into a concentrated solution of $[PtCl_2(76)]$ in dimethyl sulfoxide, under nitrogen.

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 0.81 (d, $^3J_{HH}$ = 5.6 Hz, 12H, CH_3), 0.97 (d, $^3J_{HH}$ = 5.9 Hz, 12H, CH_3), 2.78 – 2.91 (m, 4H, CH_2CH_2), 4.61 (sept, J_{HH} = 6.0 Hz, 1H, C*H*), 6.94 (t, $^3J_{HH}$ = 7.1 Hz, 4H, Ar*H*), 7.05 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 4.6 Hz, 4H, Ar*H*), 7.48 (t, $^3J_{HH}$ = 7.8 Hz, 4H, Ar*H*), 7.71 – 7.80 (m, 4H, Ar*H*).

^{31}P NMR (DMSO-d_6, ref-H_3PO_4, 121 MHz): δ = 47.6 (s, J_{PPt} = 3659 Hz).

Elemental Analysis: $C_{38}H_{48}Cl_2O_4P_2Pt.CH_2Cl_2$ calcd (%) C 47.72, H 5.13, found (%) C 48.21, H 5.35.

MS (+ESI): 919 [*M* + Na]$^+$, 861 [*M* – Cl]+.

6.6.4.3. [$PtCl_2$(77)], 157

Synthesised using the same method as [$PtCl_2$(69)], **155** with bis-(di-*ortho*-(1,3-dioxolan-2-yl)phenyl)phosphino)ethane, **77** (40 mg, 0.058 mmol) and [$PtCl_2$(COD)] (22 mg, 0.058 mmol) in dichloromethane (10 mL), giving a white solid (39 mg, 0.054 mmol, 71 %).

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.28 – 2.31 (m, 4H, C*H*$_2$C*H*$_2$), 3.75 – 3.86 (m, 8H, OC*H*$_2$C*H*$_2$O), 4.02 – 4.12 (m, 8H, OC*H*$_2$C*H*$_2$O), 5.76 (s, 4H, C*H*), 7.38 – 7.45 (m, 4H, Ar*H*), 7.65 – 7.80 (m, 12H, Ar*H*).

^{31}P NMR (DMSO-d_6, ref-H_3PO_4, 121 MHz): δ = 44.6 (s, J_{PPt} = 3646 Hz).

Elemental Analysis: $C_{38}H_{40}Cl_2O_8P_2Pt.CH_2Cl_2$ calcd (%) C 45.16, H 4.02, found (%) C 46.15, H 4.81.

MS (+ESI): 975 [*M* + Na]$^+$, 917 [*M* – Cl]$^+$.

6.6.5. Ethene Trimerisation Reactions

6.6.5.1. At Low Ethene Pressure

The general trimerisation method was adapted from a method reported by Wass and co-workers.[4] Ethene trimerisation at low ethene pressure was performed using the same method as the cotrimerisation of styrene and ethene (see Section 6.2.1), using *N*,*N*-bis(di-*ortho*-ethoxyphenylphosphino)methylamine **68** (about 5 mg, 10 μmol),

[$Cr(acac)_3$] (3.5 mg, 10 μmol), toluene (10 mL) and methylaluminoxane (MAO, 10 % wt solution in toluene, 2 mL, 300 equivalents, 3 mmol). The resulting toluene solution was analysed by GC. The same method was used for testing ligands ligand **69**, **75**, **76** and **77**.

6.6.5.2. At High Ethene Pressure

N,N-bis(di-*ortho*-ethoxyphenylphosphino)methylamine **68** (about 5 mg, 10 μmol), [$Cr(acac)_3$] (3.5 mg, 10 μmol) were loaded into a reaction cell in a Baskerville 10 multicell autoclave in an inert atmosphere glove box. The autoclave was removed from the glove box and toluene (1 mL) was added. To each cell was added methylaluminoxane (MAO, 10 % wt solution in toluene, 2 mL, 300 equivalents, 3 mmol) *via* syringe. The autoclave was closed, heated to 45 °C and placed under 40 bar of ethene. The reaction was stirred for 1 h, after which the reactor was allowed to cool to room temperature and the pressure was slowly released. Dilute hydrochloric acid (10 % solution) was added to each cell to quench the reaction. The organic layer was collected, washed with distilled water (2 x 5 mL) and then dried over magnesium sulphate. The resulting toluene solution was analysed by GC. The same method was used for testing ligands ligand **69**, **75**, **76** and **77**.

Chapter 7

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Chapter 8

Appendices

Appendix 8.1 – Cotrimerisation of Ethene with Styrenic Monomers

Shown in Figure 8.1 and 8.2 are the GC traces produced from the trimerisation of ethene and the cotrimerisation of ethene and styrene.

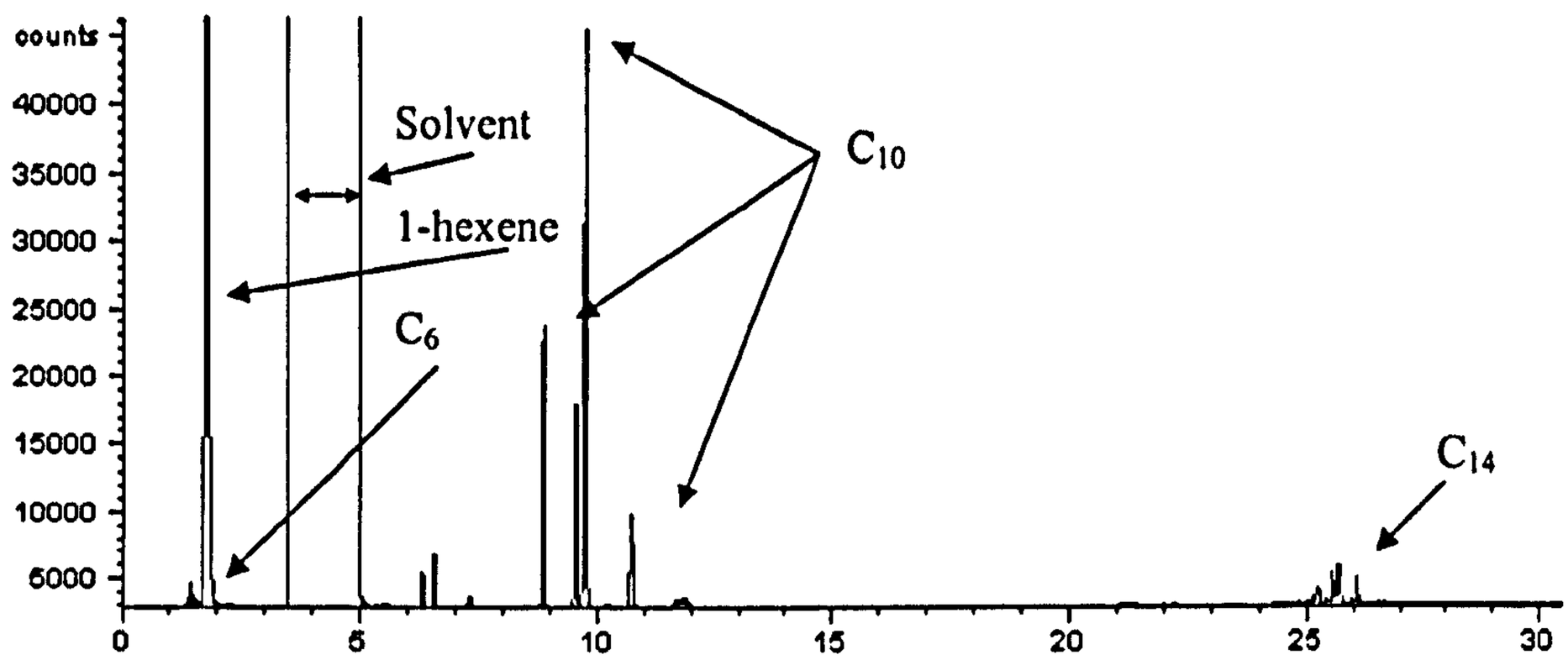


Fig 8.1 – GC Trace from Trimerisation of Ethene

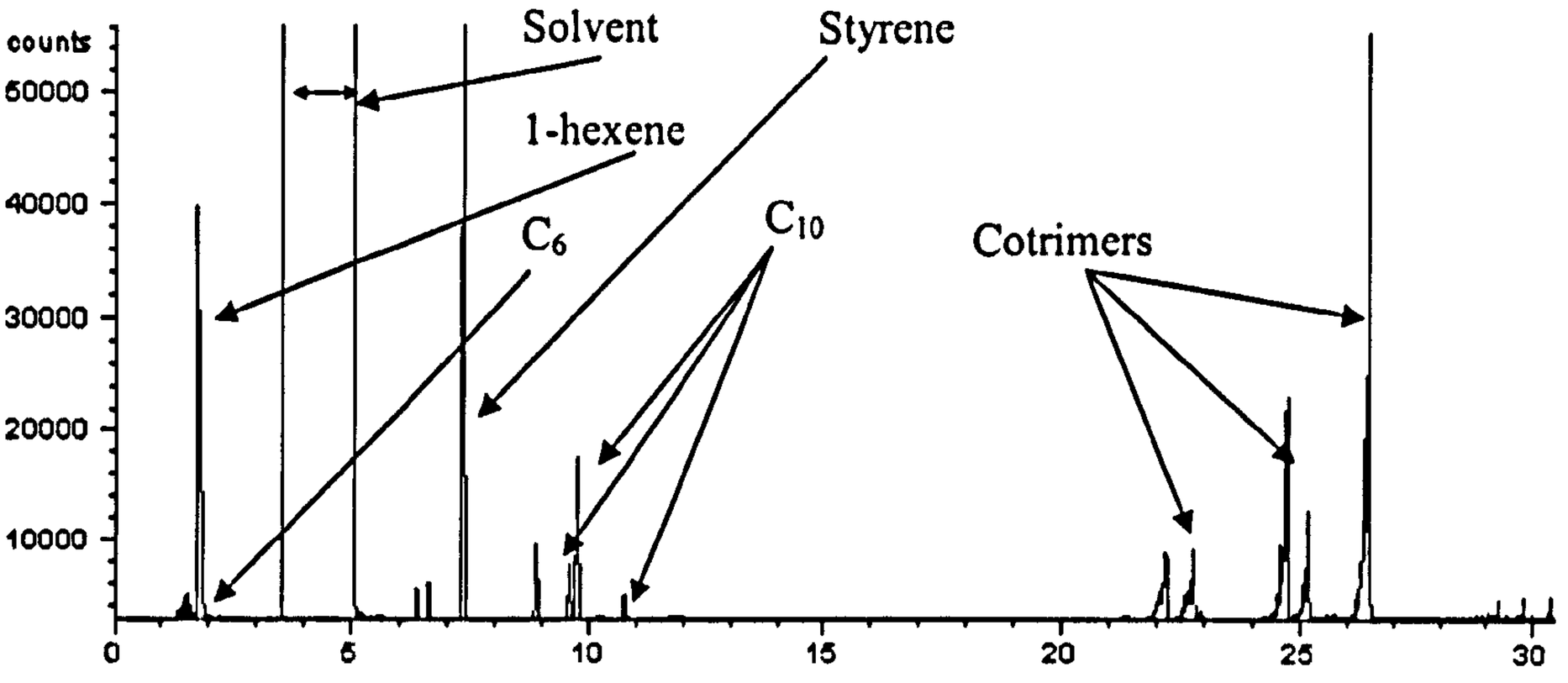


Fig 8.2 – GC Trace from Cotrimerisation of Ethene and Styrene

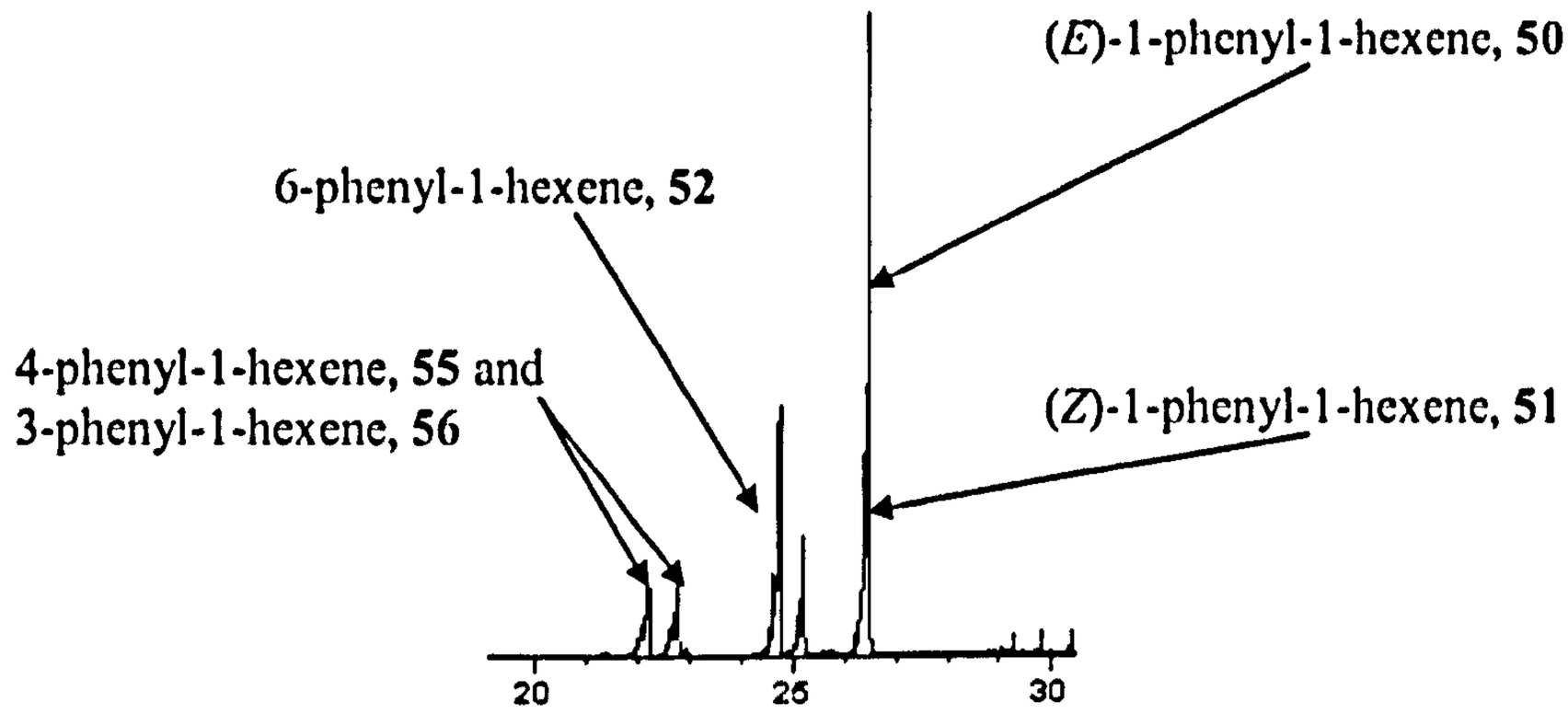


Figure 8.3 – Cotrimer Section of GC Trace Shown in Figure 8.2

Appendix 8.2 – Trimerisation of 1,3-Dienes

GC Trace

Figure 8.4 shows the GC trace given from the trimerisation of isoprene.

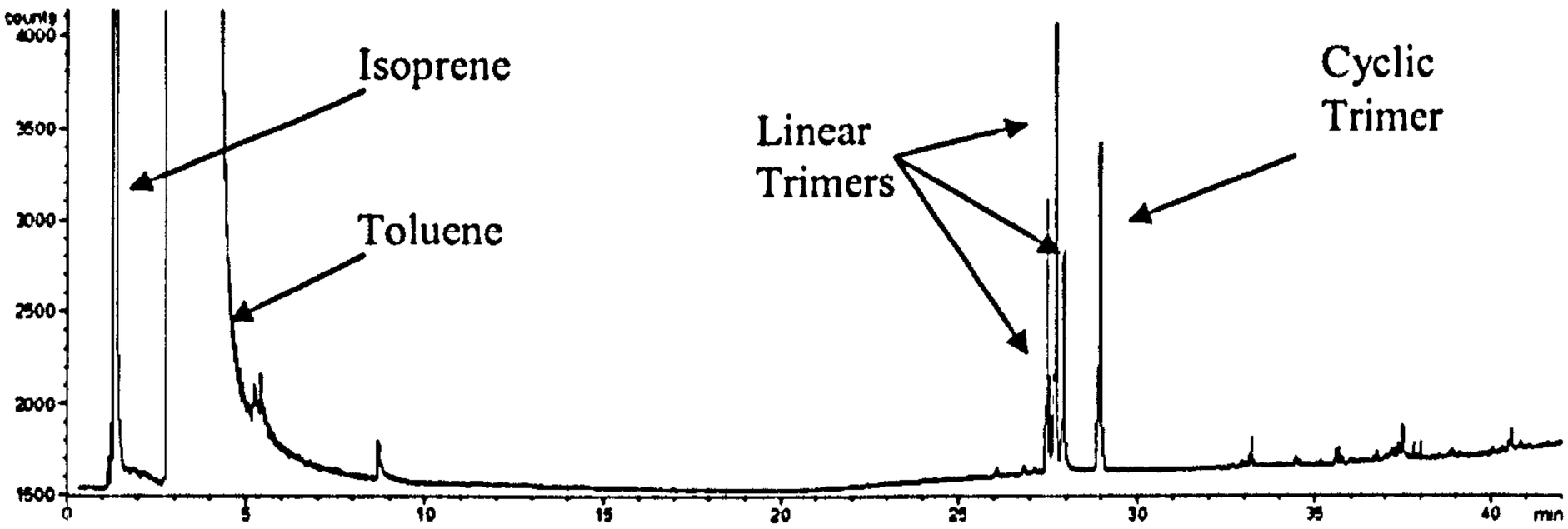
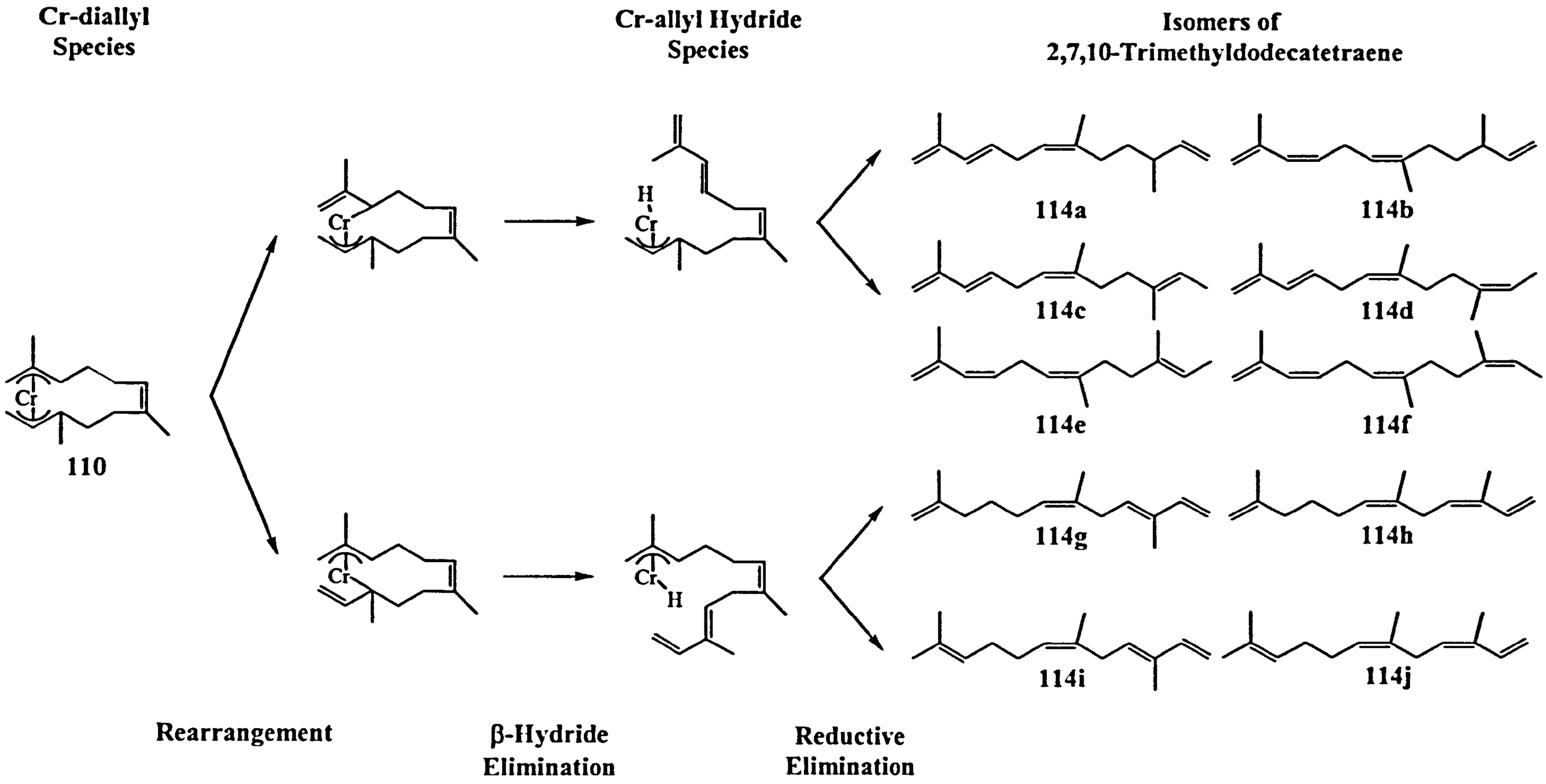


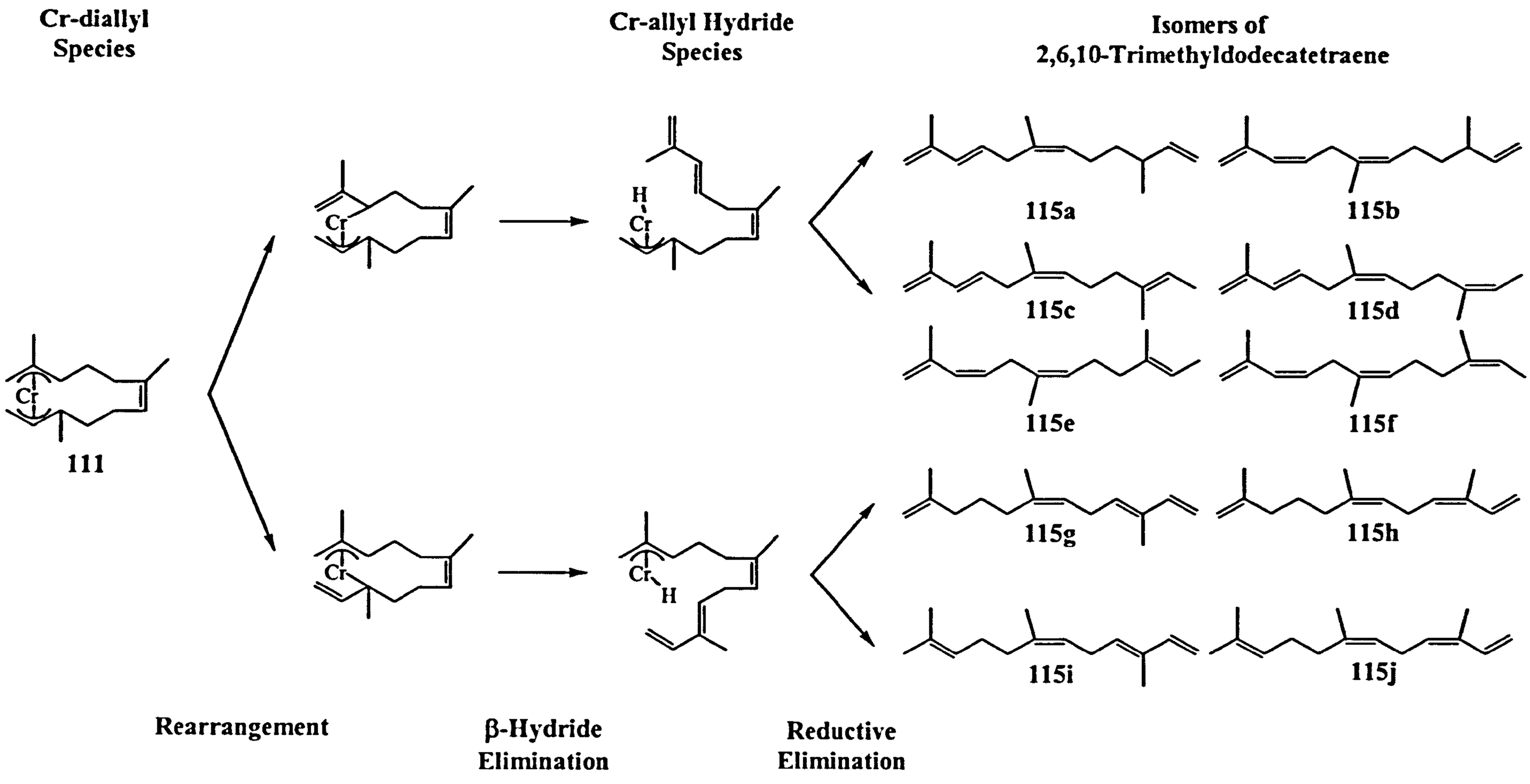
Figure 8.4 – GC Trace of Products from the Trimerisation of Isoprene

List of Isoprene Trimer Isomers

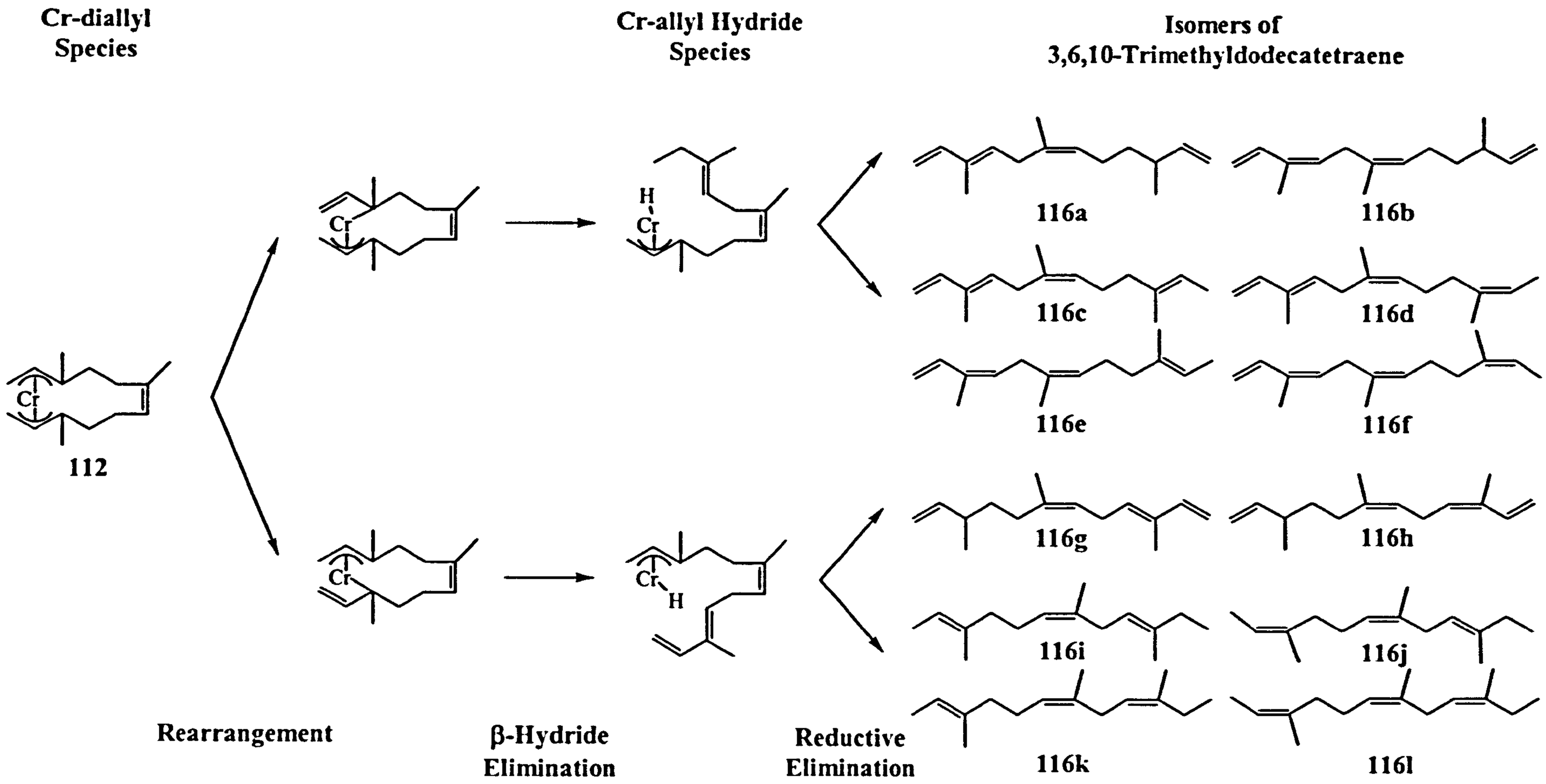
Figures 8.5 to 8.8 show the formation of each of the possible trimer products from the trimerisation of isoprene, see Scheme 3.9 for isomers of compound 113.



Scheme 8.5 – Formation of Different Isomers of 2,7,10-Trimethyldodecatetraene, 114, from Intermediate 110



Scheme 8.6 – Formation of Different Isomers of 2,6,10-Trimethyldodecatetraene, 115, from Intermediate 111



Scheme 8.7 – Formation of Different Isomers of 3,6,10-Trimethyldodecatetraene, 116, from Intermediate 112

Trimerisation of 2,3-Dimethyl-1,3-butadiene

The GC-MS trace for trimerisation of 2,3-dimethyl-1,3-butadiene is shown in Figure 8.5.

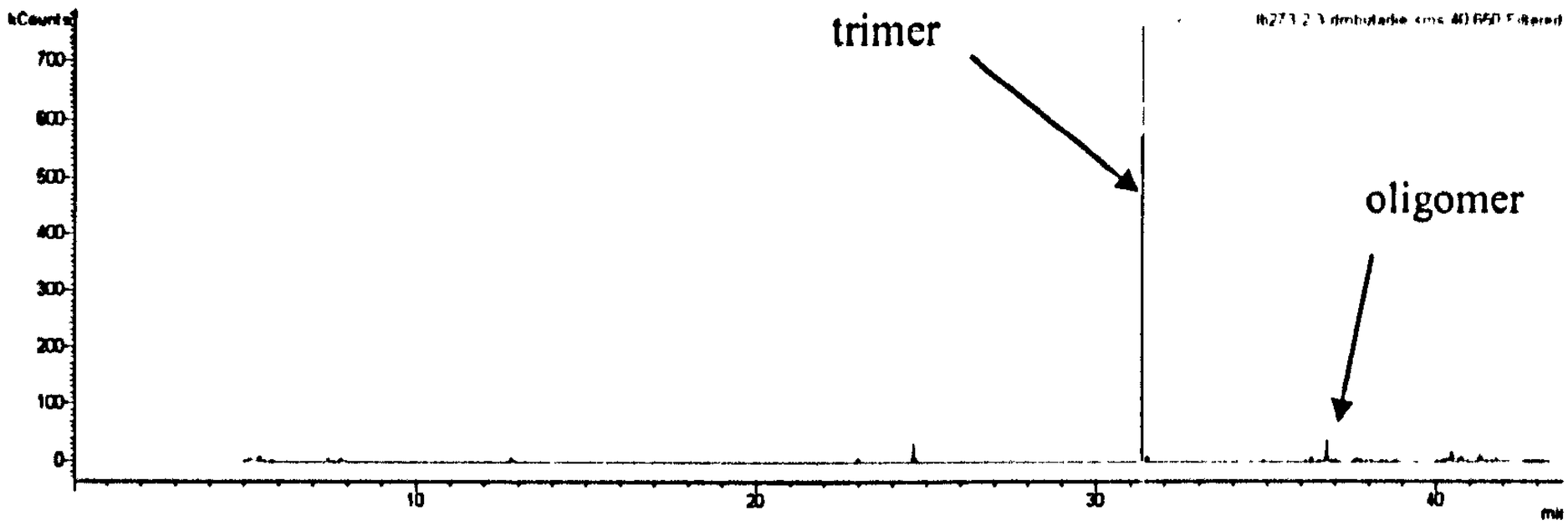


Figure 8.5 – GC-MS Trace of Products from Trimerisation of 2,3-Dimethyl-1,3-butadiene

Appendix 8.3 - Crystallographic Data

$[Cr(CO)_4(1)]$, 133

Colour, habit		Yellow Block
Size		0.48 x 0.30 x 0.07
Empirical Formula		$C_{34}H_{33}Cl_2CrNO_8P_2$
M		768.45
Crystal System		Triclinic
Space Group		P-1
a / Å		10.850(2)
b / Å		13.509(3)
c / Å		13.657(3)
α / °		76.40(3)
β / °		67.98(3)
γ / °		81.53(3)
Volume / Å^3		1788.6(8)
Z		2
Absorption Coefficient, μ / mm^{-1}		0.609
Temperature / K		173
Reflections:	Total	18942
	Independent	8213
	R_{int}	0.0526
Final R_1		0.0512
Largest Peak, hole / e Å^{-3}		1.219, -0.688

[Cr(CO)$_4$(19)], 134

Colour, habit		Pale Yellow plate
Size		0.40 x 0.40 x 0.02
Empirical Formula		$C_{31}H_{27}CrNO_4P_2$
M		591.48
Crystal System		Triclinic
Space Group		P-1
a / Å		10.795(2)
b / Å		15.430(3)
c / Å		17.984(4)
α / °		90.51(3)
β / °		106.82(3)
γ / °		95.17(3)
Volume / Å^3		2853.7(10)
Z		4
Absorption Coefficient, μ / mm^{-1}		0.55
Temperature / K		100
Reflections:	Total	32614
	Independent	13018
	R_{int}	0.0429
Final R_1		0.0515
Largest Peak, hole / e Å^{-3}		0.551, -0.350

[Cr(CO)$_4$(5)], 135

Colour, habit		Pale yellow block
Size		0.38 x 0.28 x 0.16
Empirical Formula		$C_{34}H_{32}Cl_2CrO_8P_2$
M		753.44
Crystal System		Triclinic
Space Group		P-1
a / Å		11.807(9)
b / Å		17.767(11)
c / Å		17.847(9)
α / °		80.50(6)
β / °		86.84(4)
γ / °		74.80(6)
Volume / Å^3		3563(4)
Z		4
Absorption Coefficient, μ / mm^{-1}		0.609
Temperature / K		173
Reflections:	Total	37832
	Independent	16293
	R_{int}	0.0295
Final R_1		0.0472
Largest Peak, hole / e Å^{-3}		1.015, -1.151

$[Cr(CO)_4(NO)(1)]$, 136

Colour, habit		Yellow block
Size		0.09 x 0.04 x 0.03
Empirical Formula		$C_{32}H_{31}BCrF_4N_2O_8P_2$
M		772.34
Crystal System		Monoclinic
Space Group		P $2_1/n$
a / Å		11.398(2)
b / Å		19.022(4)
c / Å		18.460(4)
α / °		90
β / °		101.33(3)
γ / °		90
Volume / Å^3		3294.2(14)
Z		4
Absorption Coefficient, μ / mm^{-1}		3.748
Temperature / K		100
Reflections:	Total	29906
	Independent	7312
	R_{int}	0.0980
Final R_1		0.0480
Largest Peak, hole / e Å^{-3}		0.445, -0.314

Bis(di-*ortho*-(1,3-dioxolan-2-yl)phenylphosphino)ethane, 77

Colour, habit		Colourless block
Empirical Formula		$C_{38}H_{40}CrO_8P_2$
M		686.64
Crystal System		Monoclinic
Space Group		P 2(1)/c
a / Å		9.635(3)
b / Å		12.360(6)
c / Å		14.313(5)
α / °		90
β / °		104.477(3)
γ / °		90
Volume / Å^3		1650.31(11)
Z		2
Absorption Coefficient, μ / mm^{-1}		0.187
Temperature / K		100
Reflections:	Total	15041
	Independent	4887
	R_{int}	0.0301
Final R_1		0.0428
Largest Peak, hole / e Å^{-3}		0.318, -0.295

$[Cr(CO)_4(68)]$, 133

Colour, habit		Pale yellow rectangular prism
Size		0.40 x 0.13 x 0.04
Empirical Formula		$C_{38}H_{41}Cl_2CrN_2O_8P_2$
M		824.56
Crystal System		Monoclinic
Space Group		P 2_1/n
a / Å		13.338(4)
b / Å		19.819(4)
c / Å		15.090(3)
α / °		90
β / °		94.245(19)
γ / °		90
Volume / Å^3		3978.10(14)
Z		4
Absorption Coefficient, μ / mm^{-1}		0.553
Temperature / K		100
Reflections:	Total	46430
	Independent	12088
	R_{int}	0.0470
Final R_1		0.0533
Largest Peak, hole / e Å^{-3}		1.022, -1.036

$[Cr(CO)_4(75)]$, 134

Colour, habit		Pale Yellow block
Size		0.42 x 0.39 x 0.26
Empirical Formula		$C_{38}H_{40}CrO_8P_2$
M		738.64
Crystal System		Triclinic
Space Group		P -1
a / Å		12.112(4)
b / Å		17.561(5)
c / Å		18.342(5)
α / °		93.118(2)
β / °		106.893(3)
γ / °		106.715(3)
Volume / Å^3		3534.55(18)
Z		4
Absorption Coefficient, μ / mm^{-1}		0.466
Temperature / K		100
Reflections:	Total	52239
	Independent	23859
	R_{int}	0.0247
Final R_1		0.0347
Largest Peak, hole / e Å^{-3}		0.459, -0.522

$[PtCl_2(76)]$, 156

Colour, habit		Colourless block
Size		0.40 x 0.36 x 0.28
Empirical Formula		$C_{38}H_{48}Cl2O_4P_2Pt$
M		896.69
Crystal System		Orthorhombic
Space Group		Pna2 (1)
a / Å		17.864(2)
b / Å		12.152(10)
c / Å		19.458(2)
α / °		90
β / °		90
γ / °		90
Volume / Å^3		4224.18(7)
Z		4
Absorption Coefficient, μ / mm^{-1}		3.558
Temperature / K		120
Reflections:	Total	67269
	Independent	13303
	R_{int}	0.0466
Final R_1		0.0354
Largest Peak, hole / e Å^{-3}		4.185, -3.333

Appendix 8.4 – Published Papers

The following section shows the papers published from the data in this thesis.

1. Selective Cotrimerization of Ethene and Styrenic Comonomers, L. E. Bowen and D. F. Wass, *Organometallics*, 2006, **25**, 555. (reference 93 in thesis)

2. The selective trimerisation of isoprene with chromium *N,N*-bis(diarylphosphino)-amine catalysts, L. E. Bowen, M. Charernsuk, D. F. Wass, *Chem. Comm.* 2007, 2835. (reference 130 in thesis)

3. One electron oxidation of chromium *N,N*-bis(diarylphosphino)amine and bis(diarylphosphino)methane complexes relevant to ethene trimerisation and tetramerisation, L. E. Bowen, M. F. Haddow, A. G. Orpen and D. F. Wass, *Dalton Trans.* 2007, 1160. (reference 160 in thesis)